# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 1

### Basic Conditions of Analysis of Atomic Absorption SPECTROPHOTOMETRY

SHIMADZU CORPORATION

## Atomic Absorption Spectrophotometer Cookbook

## Section 1

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# 1. Principal of Atomic Absorption Spectrophotometer

## 1.1 Why atoms absorb light

The atomic absorption spectrometry uses absorption of light of intrinsic wavelengths by atoms. All atoms are classified into those having low energies and those having high energies. The state having low energies is called the ground state and the state having high energies is called the excited state.

The atom in the ground state absorbs external energies and is put in the excited state. For example, sodium is mainly in two excited states, having higher energies by 2.2eV and 3.6eV respectively than in the ground state, as shown in Fig. 1.1. (eV is a unit to measure energies and is called an "electron volt".) When 2.2eV energy is given to the sodium atom in the ground state, it moves up to the excited state in (I) and when 3.6eV energy is given, it moves up to the excited state in (II).

Energy is given as light, and 2.2eV and 3.6eV respectively correspond to energy of light at 589.9nm and 330.3nm wavelength.

In the case of sodium in the ground state, only light of these wavelengths are absorbed and no other wavelength light is absorbed at all.

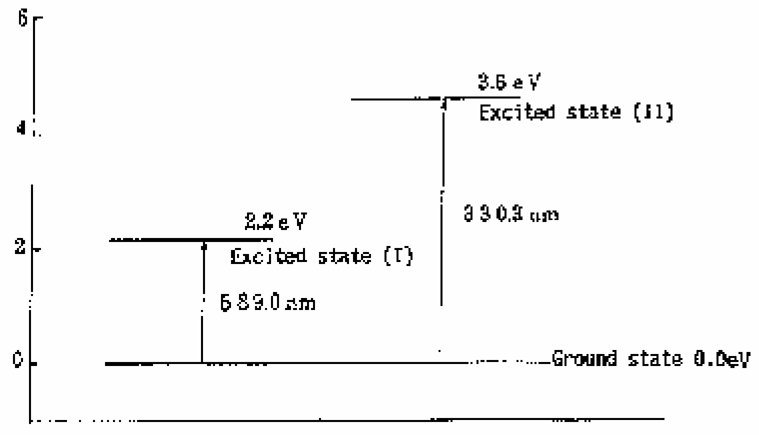


**Fig. 1.1 Sodium energy states**

The difference between energies in the ground state, and in the excited state is fixed by the element and wavelength of light to be absorbed. Atomic absorption spectrometry uses the hollow cathode lamp (HCL).

The HCL gives off light characteristic to the elemental wavelength being measured. Thus, the light absorbed measures the atomic density.

## 1.2 Relation between light absorption rate and atomic density

When light of certain intensity is given too many atoms in the ground state, part of this light is absorbed by atoms.

The absorption rate is determined by the atomic density.

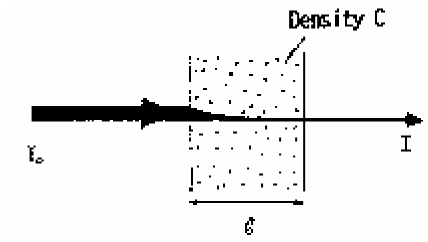


Fig. 1.2 Principle of atomic absorption

When light of $I_o$ intensity is given to density C, atoms speed in length 1 as shown in Fig. 1.2. The light is absorbed and its intensity is weakened to I. The following formula is formed between I and $I_o$.

$$I = I_o \times e^{-k \cdot l \cdot c}$$

(k: Proportional constant)

$$\text{or} - \log \frac{I}{I_o} = k \cdot l \cdot c$$

This is called the Lambert-Beer's Law, and $-\log \frac{I}{I_o}$ value is absorbance. The above formula indicates that absorbance is proportional to atomic density. When absorbance is measured on samples of 1, 2 and 3 ppm for example and plotted, a straight line is obtained as shown in Fig. 1.3. Absorbance and concentration represented graphically is called the calibration curve.

When the absorbance of an unknown sample is obtained, the concentration can be determined from the graph as shown.

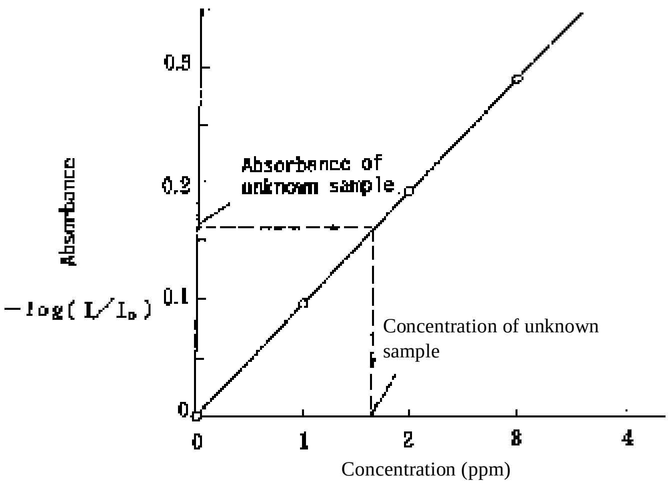


Fig. 1.3 Calibration curve

## 1.3 Sample atomization method

The principle mentioned above can be applied to light absorption of “Free atoms”. A “Free atom” means an atom not combined with other atoms. However, elements in the sample to be analyzed are not in the Free State, and are combined with other elements invariably to make a so-called molecule. For example, sodium in seawater mainly combines with chlorine to form a NaCl (Sodium chloride) molecule. Absorption cannot be done on samples in the molecule state, because molecules do not absorb light.

The combination must be cut off by some means to free the atoms. This is called atomization. The most popular method of atomization is dissociation by heat - samples are heated to a high temperature so that molecules are converted into free atoms. This method is classified into the flame method, in which a chemical flame is used as the heat source; and a flameless method, in which a very small electric furnace is used.

### a) Flame atomic absorption

The flame is produced by a burner for atomization and this is the most popular method. It is standard in almost all atomic absorption devices available on the market at present.

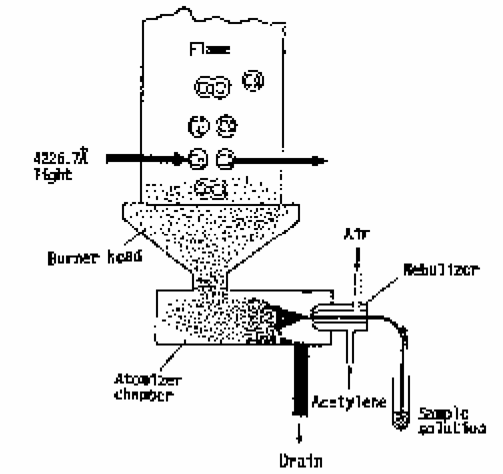


Fig. 1.4 Flame atomic absorption

A typical diagram of the burner is shown in Fig. 1.4. This figure explains measurement of calcium contained in the sample liquid as calcium chloride. The sample is atomized by a nebulizer at first. Then, big water drops are discharged to the drain, and only a fine mist is mixed with fuel and oxidant in the atomizer chamber and sent to the flame.

When they get in the flame, the mist evaporates instantaneously and fine particles of calcium chloride molecules are produced. When these particles further advance in the flame, calcium chloride is dissolved by heat and free calcium atoms and chloride atoms are produced.

If a beam of light at wavelength 422.7nm (Ca) is introduced through this part of the flame, atomic absorption can be measured. In the upper part of the flame, some of calcium atoms are combined with oxygen to become calcium oxide and some are further ionized. Therefore, atomic absorption does not show sufficient sensitivity even if light is given to such a position.

Many combinations of various gases have been tested as the flame for atomization. In consideration of analysis sensitivity, safety, easy use, cost and other points; there are four standard flames used: air-acetylene, nitrous oxide-acetylene, air-hydrogen and argon-hydrogen. These flames are used for each element depending on the temperature and gas characteristics.

**b) Electro-thermal atomic absorption**

The atomization method using a flame is still popularly used as the standard atomization method due to good reproducibility of measured values and easy use. However, a major defect of the flame method is the atomization rate out of all sample quantity used is about 1/10 and the remaining 9/10 is discharged to the drain. Therefore, it has been pointed out that atomization efficiency is low and analysis sensitivity is not so high.

Electro-thermal atomic absorption (flameless method), using a graphite tube, improves the above defects to elevate sensitivity 10 to 200 times as much. This method was originated by Dr. L'vov of Russia.

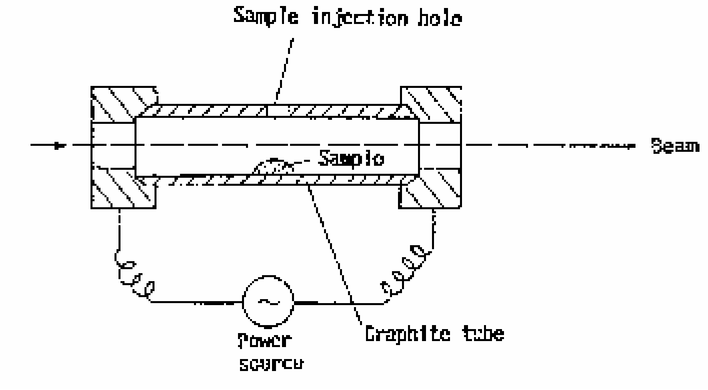


**Fig. 1.5 Flameless atomizer**

In the electro-thermal atomic absorption method, the sample is injected in the formed graphite tube and an electric current of 300 ampere (maximum) is applied to the tube. The graphite is heated to a high temperature and the elements in the sample are atomized.

If light from the light source is sent through the tube, light is absorbed when they are atomized. In an actual measurement, after the sample is injected in the tube, heating is done in three stages as shown in Fig. 1.6. That is, in the drying stage, the tube is heated to about 100°C and water in the sample evaporates completely. Then, in the ashing stage, the tube is heated to 400°C to 1000°C and organic matter and other coexistent matter dissolve and evaporate. Lastly, in the atomizing stage, it is heated to 1400°C to 3000°C and metallic salts left in the tube are atomized. Heating is usually done by changing the temperature in steps shown by the solid line in Fig. 1.6 (step heating). Depending on the sample, when the decomposition temperature of coexistent matter is close to its atomization temperature, heating is done by changing temperature continuously (ramp mode heating).

Heating must be done under the conditions (temperature, heating time, and temperature raising method), which suit the type of element and composition of the sample to be measured.

If heating is started after the optimum conditions are set on the equipment in advance, the tube is automatically heated according to the set temperature program.

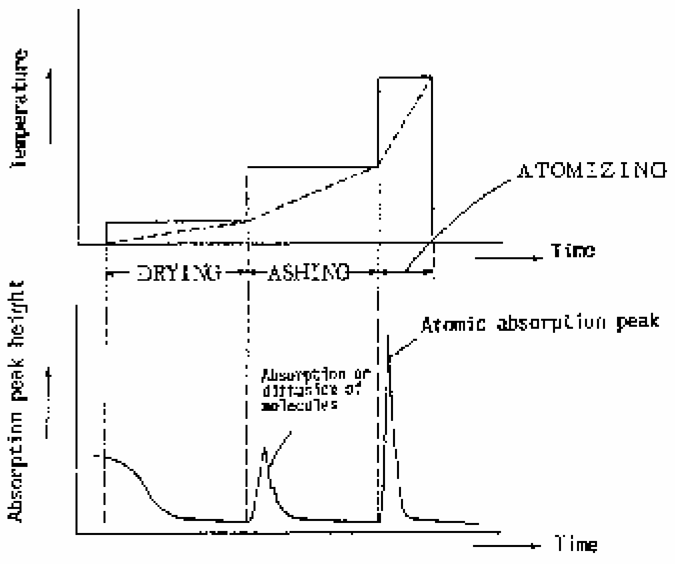


**Fig. 1.6 Heating program and absorption curve according to electro-thermal atomic absorption**

### c) Other atomic absorption methods

Methods having higher sensitivity than normal flame atomic absorption or electro-thermal atomic absorption are often used for special elements including arsenic, selenium and mercury. They use chemical reactions in the process of atomization to vaporize in the form of an atom or simple molecule.

1. **Hydride vapor generation technique**

The hydride vapor generation technique is used to make the sample react on sodium borohydride. It is acidified with HCL to reduce the object metal, and combine it with the hydrogen in order to produce a gaseous metal hydride. This gas is sent to the high temperature atomization unit for measurement.

2. **As, Se, Sb, Sn, Te, Bi, Hg and other metals produce a metal hydride by this method.**

Fig. 1.7 shows the block diagram of the hydride generating equipment. The peristalsistic pump is used to send the sample, 5M hydrochloric acid and 0.5% sodium borohydride solution to the reaction coil. The metal hydride is generated in the reaction coil and the gas-liquid separator is used to separate the gas phase and liquid phase. Argon gas is used as the carrier gas. The gas phase is sent to the absorption cell, which is heated by the air-acetylene flame, and the metallic element is atomized.

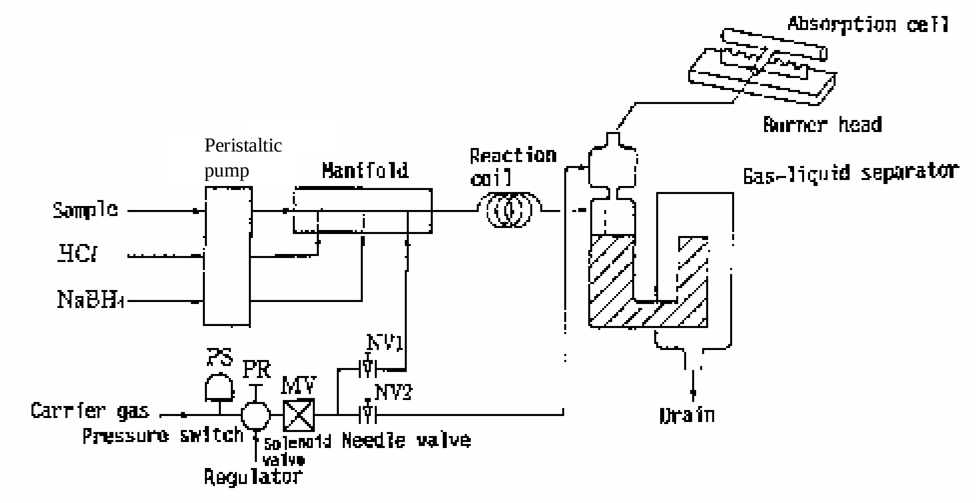


Fig. 1.7 Block diagram of hydraulic generating equipment

### 3. Reduction vapor atomization

Mercury in solution is a positive ion. When it is reduced to a neutral ion, it vaporizes as a free atom of mercury, at room temperature. Tin (II) chloride is used as a reducing agent and mercury atoms are sent to the atomic absorption equipment with air as the carrier gas.

Fig. 1.8 shows the block diagram of the mercury analysis equipment. 200m*l* of the sample is put in the reaction vessel, and tin (II) chloride is added for reduction. When air is sent to the gas flow cell through the drying tube, atomic absorption by mercury is measured.

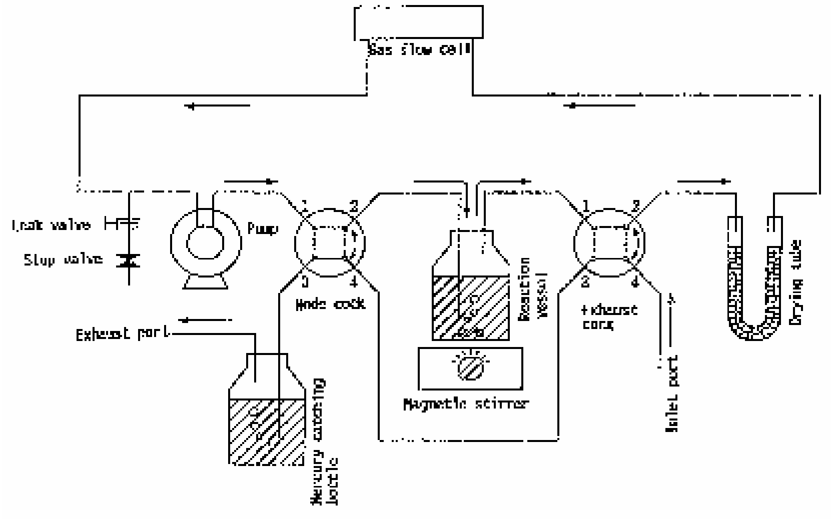


Fig. 1.8 Block diagram of mercury analysis equipment

## 2.Basic Condition for Analysis

The equipment must be set at the optimum analysis conditions to obtain the best measurement results.

Optimum conditions generally vary with the element and with the composition of the sample, even if the same elements are contained. Therefore, it is necessary to fully study the measuring conditions in actual analysis.

## 2.1 Conditions of equipment

### a) Analysis line

Light from the hollow cathode lamp shows a number of primary and secondary spectrums of cathode elements and filler gas. They are complicated particularly with 4, 5, 6, 7 and 8 families in the middle of the periodic table, showing several thousand spectrums.

Parts of many spectral lines contribute to atomic absorption. The atomic absorption analysis selects and uses the spectral line of the biggest atomic absorbance.

The spectral line having absorption sensitivity suitable for the analysis may be used. This depends on the concentration range where the elements in the sample are measured.

An element may have two or more spectral lines showing atomic absorption as in Table 2.1. It is desirable to check absorption sensitivity and emission intensity of these spectral lines. Also, study the concentration range in which each wavelength is measured in order to avoid the dilution error when the concentration is high as in the main component analysis.

## Table 2.1 Analysis lines and absorption sensitivities

(Characteristics of hollow cathode lamp and handling method

Hamamatsu Photonics)

| Elements | Analysis line wavelength (nm) | Absorption sensitivity | Flame type |
|---|---|---|---|
| Ag | 328.07 | 10 | Air-$C_2H_2$ |
| | 338.29 | 5.3 | |
| Al | 309.27 | 10 | $N_2O$-$C_2H_2$ |
| | 396.15 | 8.6 | |
| | 237.13<br>237.30 | 2.0 | |
| As | 193.70 | 10 | Ar-$H_2$ |
| | 197.20 | 6.2 | |
| | 189.00 | 5.0 | |
| Au | 242.80 | 10 | Air-$C_2H_2$ |
| | 267.59 | 5.5 | |
| B | 249.68<br>249.77 | 10 | $N_2O$-$C_2H_2$ |
| | 208.89 | 8.2 | |
| Ba | 553.55 | 10 | $N_2O$-$C_2H_2$ |
| | 350.11 | 0.01 | |
| Be | 234.86 | 10 | $N_2O$-$C_2H_2$ |
| Bi | 223.06 | 10 | Air-$C_2H_2$ |
| | 222.83 | 3.0 | |
| | 306.77 | 2.5 | |
| Ca | 422.67 | 10 | Air-$C_2H_2$ |
| | 239.86 | 0.05 | |
| Cd | 228.80 | 10 | Air-$C_2H_2$ |
| | 326.11 | 0.02 | |
| Co | 240.73 | 10 | Air-$C_2H_2$ |
| | 251.98 | 4.4 | |
| | 243.58 | 1.3 | |
| | 346.58 | 0.5 | |
| Cr | 357.87 | 10 | Air-$C_2H_2$ |
| | 425.44 | 4.4 | |
| | 427.88 | 2.7 | |
| | 428.97 | 1.0 | |
| Cs | 852.11 | 10 | Air-$C_2H_2$ |
| Cu | 324.75 | 10 | Air-$C_2H_2$ |
| | 327.40 | 4.7 | |
| | 217.89 | 1.2 | |
| | 218.17 | 1.0 | |
| | 222.57 | 0.6 | |
| Dy | 404.59 | 10 | $N_2O$-$C_2H_2$ |
| | 421.17 | 8.9 | |
| | 418.68 | 8.0 | |
| Er | 400.79 | 10 | $N_2O$-$C_2H_2$ |
| | 415.11 | 5.9 | |
| | 386.28 | 5.5 | |
| Eu | 459.40 | 10 | $N_2O$-$C_2H_2$ |
| | 462.72 | 8.7 | |
| | 466.19 | 7 | |
| Fe | 248.33 | 10 | Air-$C_2H_2$ |
| | 271.90 | 2.7 | |
| | 371.99 | 0.9 | |
| | 385.99 | 0.6 | |
| Ga | 294.36 | 10 | Air-$C_2H_2$ |
| | 287.42 | 8.2 | |
| | 403.30 | 4.2 | |
| Gd | 407.89 | 10 | $N_2O$-$C_2H_2$ |
| | 422.59 | 10 | |
| | 378.31 | 10 | |
| Ge | 265.16 | 10 | $N_2O$-$C_2H_2$ |
| | 270.96 | 4.8 | |
| | 269.13 | 3.0 | |
| Hf | 286.64 | 10 | $N_2O$-$C_2H_2$ |
| | 307.29 | 9.3 | |
| | 289.83 | 5.0 | |
| Hg | 253.65 | 10 | Reduction vaporization |

| Elements | Analysis line wavelength (nm) | Absorption sensitivity | Flame type |
|---|---|---|---|
| Ho | 410.38 | 10 | $N_2O$-$C_2H_2$ |
|  | 416.30 | 5.8 |  |
| In | 303.94 | 10 | Air-$C_2H_2$ |
|  | 325.61 | 9.4 |  |
|  | 410.48 | 4.0 |  |
| Ir | 208.88 | 10 | Air-$C_2H_2$ |
|  | 266.47 | 2.6 |  |
|  | 284.97 | 1.5 |  |
| K | 766.49 | 10 | Air-$C_2H_2$ |
|  | 769.90 | 2.5 |  |
|  | 404.41 | 0.03 |  |
| La | 550.13 | 10 | $N_2O$-$C_2H_2$ |
|  | 403.72 | 2.3 |  |
|  | 357.44 | 0.8 |  |
|  | 364.95 | 0.5 |  |
| Li | 670.78 | 10 | Air-$C_2H_2$ |
|  | 323.26 | 0.06 |  |
| Lu | 331.21 | 10 | $N_2O$-$C_2H_2$ |
|  | 328.17 | 7.1 |  |
| Mg | 285.21 | 10 | Air-$C_2H_2$ |
|  | 202.58 | 0.9 |  |
| Mn | 279.48 | 10 | Air-$C_2H_2$ |
|  | 280.11 | 4.7 |  |
|  | 403.08 | 1.1 |  |
| Mo | 313.26 | 10 | Air-$C_2H_2$ |
|  | 319.40 | 4.7 |  |
|  | 320.88 | 0.8 |  |
| Na | 589.00 | 10 | Air-$C_2H_2$ |
|  | 589.59 | 4.8 |  |
|  | 330.23<br>330.30 | 0.02 |  |
| Nb | 334.91 | 10 | $N_2O$-$C_2H_2$ |
|  | 405.89 | 8 |  |
| Nd | 492.45 | 10 | $N_2O$-$C_2H_2$ |
|  | 463.42 | 0.8 |  |
| Ni | 232.00 | 10 | Air-$C_2H_2$ |
|  | 341.48 | 5.1 |  |
|  | 352.45 | 5.0 |  |
|  | 231.10 | 2.0 |  |
|  | 351.50 | 0.9 |  |
| Os | 290.90 | 10 | $N_2O$-$C_2H_2$ |
|  | 305.86 | 4.5 |  |
|  | 263.71 | 4.0 |  |
|  | 330.16 | 2.0 |  |
| Pb | 217.00 | 10 | Air-$C_2H_2$ |
|  | 283.33 | 3.9 |  |
|  | 261.41 | 0.2 |  |
|  | 202.20 | 0.1 |  |
| Pd | 244.79 | 10 | Air-$C_2H_2$ |
|  | 247.64 | 6.8 |  |
|  | 276.31 | 2.2 |  |
|  | 340.46 | 1.5 |  |
| Pr | 495.13 | 10 | $N_2O$-$C_2H_2$ |
|  | 513.34 | 6.9 |  |
|  | 504.55 | 2.5 |  |
| Pt | 265.95 | 10 | Air-$C_2H_2$ |
|  | 292.98 | 2.0 |  |
| Rb | 780.02 | 10 | Air-$C_2H_2$ |
|  | 794.76 | 4.6 |  |
| Re | 346.05 | 10 | $N_2O$-$C_2H_2$ |
|  | 346.47 | 5.3 |  |
|  | 345.19 | 3.5 |  |
| Rh | 343.49 | 10 | Air-$C_2H_2$ |
|  | 339.69 | 2.8 |  |
|  | 328.09 | 0.2 |  |
| Ru | 349.89 | 10 | Air-$C_2H_2$ |

| Elements | Analysis line wavelength (nm) | Absorption sensitivity | Flame type |
|---|---|---|---|
| Sb | 217.58 | 10 | Air-$C_2H_2$ |
| | 206.83 | 7.0 | |
| | 231.15 | 3.6 | |
| | 212.74 | 1.0 | |
| Sc | 391.18 | 10 | $N_2O$-$C_2H_2$ |
| | 390.74 | 7.6 | |
| | 402.37 | 7.0 | |
| | 402.04 | 5.0 | |
| | 326.99 | 3.0 | |
| Se | 196.03 | 10 | Ar-$H_2$ |
| | 203.99 | 2.0 | |
| Si | 251.61 | 10 | $N_2O$-$C_2H_2$ |
| | 250.69 | 3.0 | |
| | 251.43 | 3.0 | |
| | 252.41 | 2.5 | |
| | 288.16 | 0.7 | |
| Sm | 429.67 | 10 | $N_2O$-$C_2H_2$ |
| | 484.17 | 8.2 | |
| Sn | 224.61 | 10 | Air-$C_2H_2$ |
| | 286.33 | 6.2 | |
| | 233.48 | 6.0 | |
| Sr | 460.73 | 10 | Air-$C_2H_2$ |
| | 407.77 | 0.6 | |
| Ta | 271.47 | 10 | $N_2O$-$C_2H_2$ |
| | 264.75 | 5.9 | |
| | 275.83 | 2.6 | |
| Tb | 432.64 | 10 | $N_2O$-$C_2H_2$ |
| | 431.88 | 8.5 | |
| | 390.14 | 6.0 | |

| Element | Analysis line wavelength (nm) | Absorption sensitivity | Flame type |
|---|---|---|---|
| Te | 214.27 | 10 | Air-$C_2H_2$ |
| | 225.90 | 1.0 | |
| Ti | 364.27 | 10 | $N_2O$-$C_2H_2$ |
| | 365.35 | 9.0 | |
| | 398.98 | 4.0 | |
| T*l* | 276.78 | 10 | Air-$C_2H_2$ |
| | 377.57 | 4.2 | |
| Tm | 371.79 | 10 | $N_2O$-$C_2H_2$ |
| | 410.58 | 6.5 | |
| | 374.41 | 6 | |
| V | 318.40 | 10 | $N_2O$-$C_2H_2$ |
| | 306.64 | 3.8 | |
| | 305.63 | 3.0 | |
| W | 255.14 | 10 | $N_2O$-$C_2H_2$ |
| | 400.87 | 3.6 | |
| | 407.44 | 0.1 | |
| Y | 410.23 | 10 | $N_2O$-$C_2H_2$ |
| | 412.83 | 8.5 | |
| | 407.74 | 8 | |
| Yb | 398.79 | 10 | $N_2O$-$C_2H_2$ |
| | 346.43 | 3.2 | |
| | 246.45 | 2.0 | |
| Zn | 213.86 | 10 | Air-$C_2H_2$ |
| | 307.59 | 0.002 | |
| Zr | 360.12 | 10 | $N_2O$-$C_2H_2$ |

**b) Slit width**

Concerning spectral lines emitted from the hollow cathode lamp, their wavelength is an independent line or complicated nearby line depending on the element.

Calcium and magnesium have no other spectral lines near the object analysis line as shown in Fig. 2.1. In case of such analysis lines, slit width is set considerably greater to obtain sufficient energy.

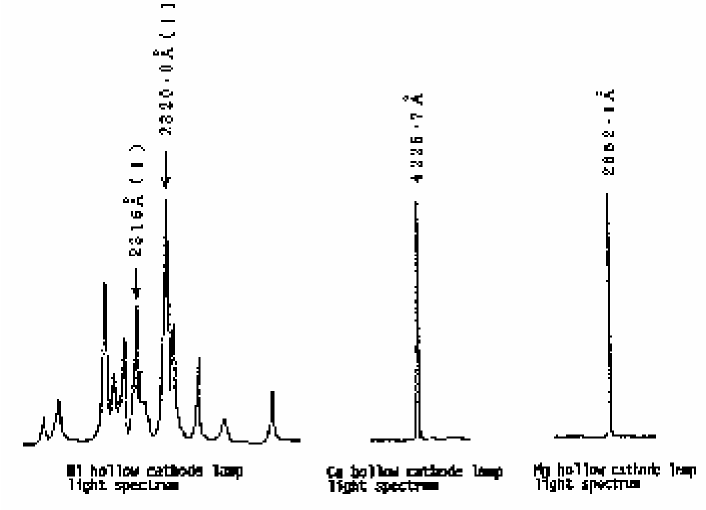


**Fig. 2.1 Lamp spectrums**

Nickel has many spectral lines near the object analysis line of 232.0nm (2320A). Because light of these nearby wavelengths is hardly absorbed with nickel atoms, the resolving power spectroscope must be increased (slit width is narrowed) to separate only 232.0nm light.

If measurement is made in the low resolving power condition, the measurement sensitivity grows worse and at the same time, linearity of the calibration curve becomes deteriorated. (Fig. 2.2)

Cobalt (Co), iron (Fe), manganese (Mn) and silicon (Si) show complicated spectrums like nickel.

The resolving power of the spectroscope must be below 2A to measure these elements accurately.

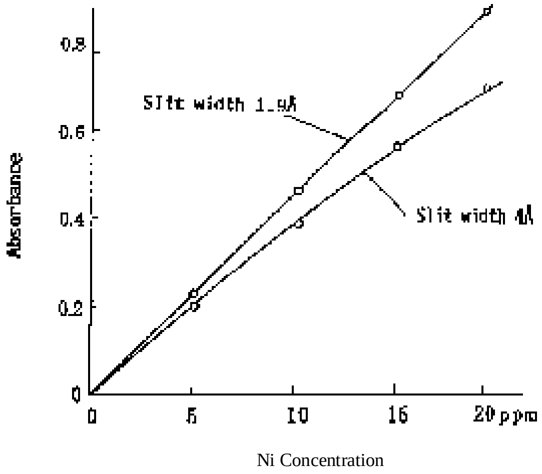


**Fig. 2.2 Slit width and calibration curve**

### c)Lamp current value

If the hollow cathode lamp operating conditions are not proper, the spectral line causes a Doppler broadening or broadening due to self-absorption, to affect the measured value. Doppler broadening is caused by the temperature of the hollow cathode lamp space, which does not contribute to lamp emission. As the hollow cathode lamp current increases, luminance increases; thus, the spectral lines broaden causing absorption sensitivity to drop as shown in Fig. 2.3.

The life of the hollow cathode lamp is generally indicated by ampere-hour (A.Hr). Therefore, the life is shortened if the current value is increased.

Such being the case, a low cathode lamp lighting current value is desirable but luminance drops if it is too low. Detector sensitivity must be increased, but noise results from it.

The lamp current value is determined by three factors: luminance (noise) of the above lamp, absorption sensitivity, and lamp life.

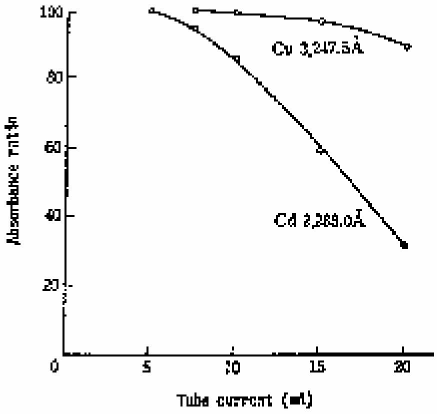


**Fig. 2.3 Sensitivity by changing the hollow cathode lamp current value**

## 2.2 Analysis conditions of flame atomic absorption

### a) Flame selection

Air-acetylene, air-hydrogen, argon-hydrogen, and nitrous oxide-acetylene are the standard types of flames used in atomic absorption analysis.

These flames vary in temperature, reducibility and transmission characteristics. The optimum flame must be selected according to the element being analyzed, and properties of the sample.

**Air-acetylene flame (AIR-$C_2H_2$)**

This flame is most popularly used and about 30 elements can be analyzed by this.

**Nitrous oxide-acetylene flame ($N_2O$-$C_2H_2$)**

This flame has the highest temperature among flames used for atomic absorption. Aluminum, vanadium, titanium, etc. combine strongly with oxygen in the air-acetylene flame and other relatively low temperature flames. Free atoms decrease and make measurement difficult. However, such elements are hard to combine with oxygen due to high temperature in the nitrous oxide-acetylene flame making satisfactory measurement possible.

The nitrous oxide-acetylene flame can also be substituted for the elements analyzed by the air-acetylene flame. The high temperature of the nitrous oxide-acetylene flame has very small interferences.

### Air-hydrogen flame (Air-$H_2$) and argon-hydrogen flame (Ar-$H_2$)

The hydrogen flame absorbs very little light from the cathode lamp, only in the short wavelength region. (Refer to Fig. 2.4).

Therefore, measurement can be done with a smaller background noise, in this short wavelength region, than with the air-acetylene flame. Those wavelength elements are As, Se, Zn, Pb, Cd, Sn, etc.

Since the argon-hydrogen, flame absorbs the smallest amount of light from 200nm and below, it is typically used.

The disadvantage of using a hydrogen type flame is that it is susceptible to interferences due to its low temperature.

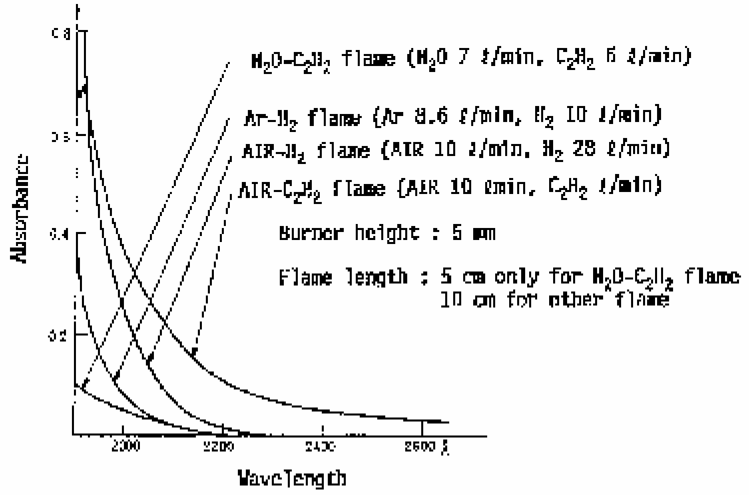


Fig. 2.4 Light absorbance of various flames

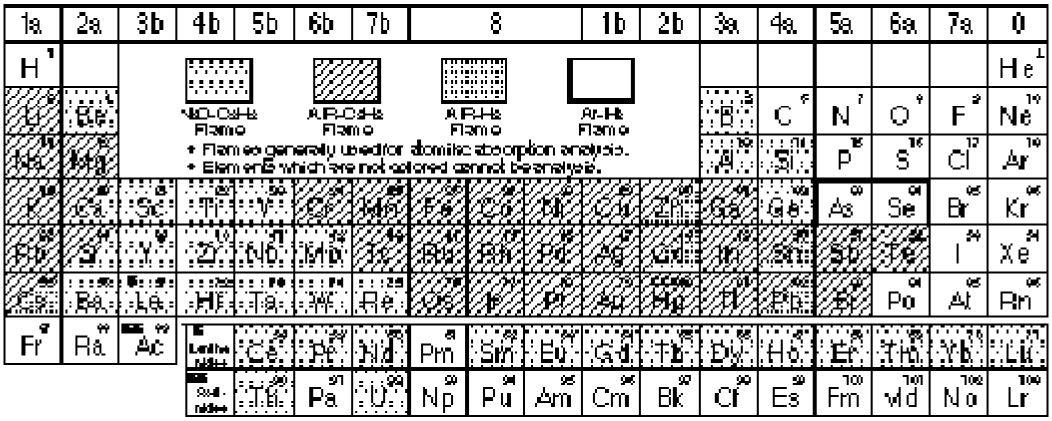
Table 2.2 shows the maximum temperature of each flame.

Table 2.3 shows elements and types of flames used.

## Table 2.2 Flame temperature

| Flame type | Maximum temperature |
|---|---|
| Argon-hydrogen | 1577°C |
| Air-hydrogen | 2045°C |
| Air-acetylene | 2300°C |
| Nitrous oxide-acetylene | 2955°C |

## Table 2.3 Elements and flames used for measurement



*** Hg is analyzed by the cold vapor mercury technique.

### b) Mixing ratio of oxidant and fuel gas

The mixing ratio of oxidant and fuel gas is one of the most important items among measurement conditions of atomic absorption analysis. The mixing ratio affects flame temperature and environment, and determines generating conditions of ground state atoms.

Therefore, the flame type as well as the beam position in the flame described in the next paragraph, control 80 to 90 percent of absorption sensitivity and stability (reproducibility). Cu, Ca, Mg, etc. increase sensitivity in the oxidizing flame containing more oxidant (fuel lean flame) and Sn, Cr, Mo, etc. increase sensitivity in the reducing flame containing more fuel gas (fuel rich flame).

Because extremely fuel lean or fuel rich may cause instability, it must be set at the optimum value depending on the target object. Absorption values by changing the acetylene flow are measured with constant airflow and the condition showing the maximum absorption value is obtained. Because the above study is concerned with the burner position described in the next paragraph, acetylene flow and burner height are adjusted to decide the optimum mixing ratio.

### c) Beam position in flame

Distributions of ground state atoms generated in the flame are not uniform depending on the element, but varies depending on the flame-mixing ratio. Fig. 2.5 shows distribution of ground state atoms when the gas-mixing ratio is changed in the measurement of chromium. It indicates that atom distribution and density change when the mixing ratio is changed. Because absorption sensitivity changes with the beam position in the flame, the burner position is set so that the beam passes the optimum position.

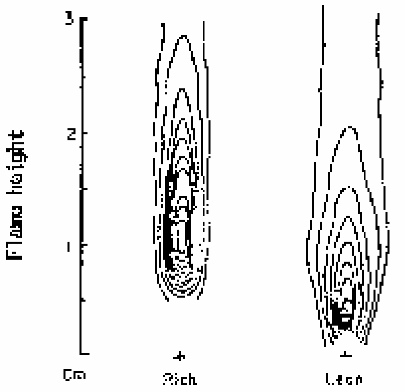


**Fig. 2.5 Distribution of chromium atoms in air-acetylene flame**
(Atomic absorption spectroscopy, W, salvin)

## 2.3 Analysis conditions of electro-thermal (flameless) atomic absorption

Electro-thermal (flameless) atomic absorption conducts heating in three basic stages for sample atomization.

The first step is the Drying Stage, which evaporates the solvent.

The second step is the Ashing Stage; to dissolve organic matter in the sample and evaporate the salts.

The third step is the Atomization Stage. If needed, a Cleaning Stage can be set. The following describes each condition setting.

### a) Drying condition

This stage is to evaporate the solvent. The heating temperature and time are set depending on the type and quantity of the solvent used for measurement.

The standard heating temperature for evaporating the solvent is 60°C to 150°C for water-type samples, or 50°C to 100°C for organic-type samples.

The heating time is based on 1 second per 1μ*l* of the sample. The heating temperature and time are set so that the solvent is evaporated completely. If the drying condition is not perfect, a fizzle (bumping) is heard or smoke blows through the graphite tube hole when the next stage is entered. To clearly examine, set the measurement mode to the deuterium lamp mode, and check if the absorption peak is exactly zero. The above is the judgment criteria.

There are two heating methods: Step and Ramp modes. In the step mode, the furnace is directly heated to the target temperature, at the beginning of the stage, and maintained at a constant temperature until the end of the stage. In the ramp mode, heating is performed at a constant rate so that the target temperature is reached by the end of the stage. The sample injected in the graphite tube diffuses (spreads) in the tube. If too much sample is injected or sample viscosity is high, the sample may stay on the surface of the graphite tube.

If sharp heating is done, the sample bubbles or bumps. When bubbling or bumping occurs, the sample flies off from the filler port and diffuses at random in the tube, making reproducibility worse.

In such a case, it is effective to make heating by step mode at a slightly lower temperature than the solvent evaporating temperature. However, ramp mode heating is easier to set the condition. Ramp mode heating and step mode heating may be combined to increase the drying efficiency.

The pyrolytic graphite tube has small filtration due to its fine surface. Therefore, special care is necessary. Spreading conditions of the sample into the tube varies with the graphite tube temperature and sample injection to worsen reproducibility. Therefore, it is desirable to inject the sample under the constant temperature of 10 to 15$^{o}$C higher than room temperature.

**b) Ashing condition**

If organic matter, or salts, exists in the atomization stage, background absorption (chemical interference) occurs giving an error in the analysis value.

Therefore, organic matter and salts are evaporated in the ashing stage where possible.

It is desirable to increase the ashing temperature as high as possible to remove organic matter and salts.

However, if the ashing temperature is increased, evaporation of the target metal happens and errors in the analysis values occur. Therefore, it must have a limit. The volatilization (evaporation) temperature of the target metal is checked in advance to decide the ashing temperature.

Fig. 2.6 shows the relation between the ashing temperature and absorption sensitivity of a lead solution with nitric acid. The ashing temperature and absorption sensitivity every 100$^{o}$C suggest that volatilization occurs from 500$^{o}$C in the case of lead.

The condition is studied on lead nitrate, but the volatilizing temperature must be checked on the same chemical species as the sample to be measured. That is because the volatilizing temperature varies with the chemical species of the target metal generated in the ashing stage.

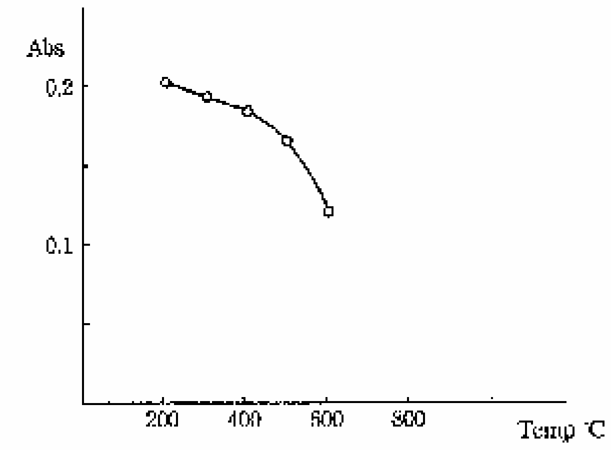


**Fig. 2.6 Relation between lead ashing temperature and sensitivity**

Background absorption decreases as the ashing temperature rises. Fig. 2.7 shows background absorption at the lead wavelength of 1/10 diluted whole blood solution, as one example, to show background tendency.

As the ashing temperature rises to 300, 400 and 500°C, background absorption decreases but is not lost completely. Therefore, a higher ashing temperature is desirable. It is assumed that lead starts volatilization at the ashing temperature 500°C as shown in Fig. 2.6 and the ashing temperature of lead cannot be raised above 500°C.

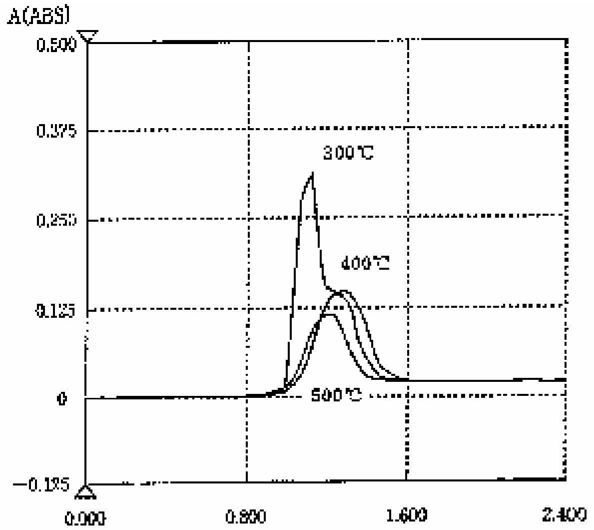


**Fig. 2.7 Relation between ashing temperature and background absorption**

One means to decrease background absorption is to dilute the sample, but it cannot be applied when density of the target metal is very low. A matrix modifier is used in such a case. Palladium (II) nitrate and nickel nitrate are used as the matrix modifier. They have the effect of increasing the volatilizing temperature of the target metal as mentioned in 5.3. That is, because the ashing temperature can be raised, background absorption can be decreased and absorption sensitivity can be increased.

Step mode heating and ramp mode heating are available as the heating method in the same way as drying. In step mode heating, salts in the graphite tube may blow out from the sample filler port after completion of drying. Generally, the method combined with ramp mode heating and step mode heating; ramp heating is done from drying temperature to ashing temperature, taking 10 to 20 seconds and then the ashing temperature is kept for the specified time.

Heating time in the ashing stage varies with the quantity of salt, or organic matter contained in the sample, and is generally 30 to 60 seconds. Whether ashing is perfect or not for this heating time can be checked by magnitude of background absorption. The deuterium lamp mode is set as the measuring mode and absorption peak in the atomizing stage is measured. The time when absorption magnitude does not change, even if the ashing time is extended, is the setting time.

c) **Atomizing condition**

This step is to atomize the target metal. Heating may be made for about 5 seconds at a slightly higher temperature than the atomizing temperature of the target metal. Absorption sensitivity, when the atomizing temperature is changed, is checked to decide the atomizing temperature. Fig. 12.8 shows the relation between the atomizing temperature and absorption sensitivity. It indicates that heating may be done at 2500°C or above.

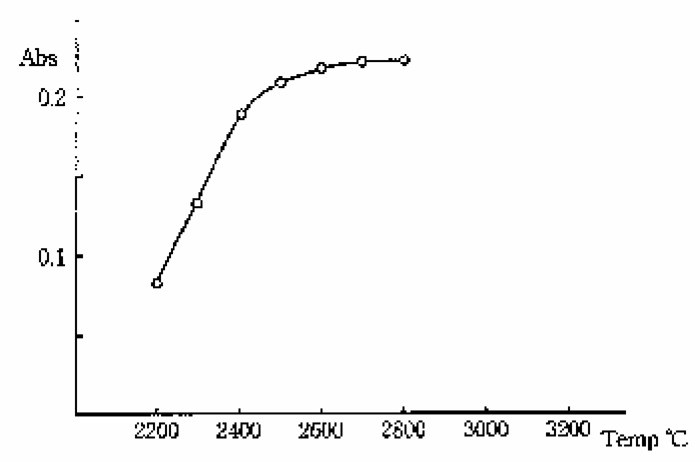


**Fig. 2.8 Relation between aluminum atomizing temperature and sensitivity**

If the atomizing temperature is set too high for metals of low melting points including cadmium and lead, the atom staying time in the tube becomes extremely short and sensitivity may drop. Metals including boron, molybdenum and calcium are easily maintained in the graphite tube. Therefore, atomization is done at a temperature as high as possible or pyrolytic graphite tube is used.

About 1*l*/min of argon is run through the graphite tube in the drying and ashing stages. If argon gas is run in the atomizing stage, sensitivity drops sharply.

Therefore, argon is stopped. Sensitivity can be adjusted five times as much by changing argon flow from 0 to 1.5*l*/min to adjust absorption sensitivity.

Step heating is generally used. When background absorption at the atomization stage is big, atomic absorption, background absorption, and measurement should be made by ramp heating.

The heating time is set so that the atomic absorption peak returns to 0 levels within the heating time. However, when the metal is easy to stay in the graphite tube or background absorption is big and does not return to 0 levels, the time when the peak returns to the specified level is set as heating time, and cleaning is done thereafter.

Cleaning is done to evaporate metal and salt, which remains in the graphite tube, at the end of the atomizing stage. Heating can be done sufficiently for 2 to 3 seconds at the maximum temperature of 3000$^{o}$C but lower temperature is desirable where possible.

The standard cleaning temperature is the atomization temperature plus 200$^{o}$C. Cleaning is done at about 2500$^{o}$C for cadmium and lead, which have low atomization temperatures.

**d) Sample injection quantity**

Proportional relations do not work between the sample quantity injected in the graphite tube and absorption sensitivity. This is because the diffusion area in the tube and filtration depth varies with sample injection quantity. Therefore, the calibration line can be prepared by changing the injection quantity of the standard solution from the specified density.

Solutions of different densities are injected in the specified quantity at one time. The injection quantity of the standard sample is naturally the same as that of the sample.

The maximum sample injection quantity is 50μ*l* but diffusion and filtering depth vary with a difference in physical properties of the sample. It spreads to the low temperature part, or overflows to the filler port often dropping analysis accuracy. Therefore, 10 to 20μ*l* is ideal.

# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 2

Standard Sample Preparation Method

Preparation of Calibration Curve and Determination Method

Interference in Atomic Absorption Spectrophotometry

SHIMADZU CORPORATION

## Atomic Absorption Spectrophotometer Cookbook

## Section 2

# CONTENTS

# 3. Standard Sample

## 3.1 Stock standard

The standard samples used for atomic absorption metals or salts dissolved in acid. When it is stored for a long period it is precipitated, or absorbed by the container wall due to hydroxide and carbonate produced, and its concentration changes.

The standard solutions available on the market are supplied in accordance with the standard solution examination system. It is based on the national standard, and is acid or alkaline.

The guarantee period of one to two years is shown and it must be used within this period.

The stock solution prepared by the standard solution method is a highly concentrated solution that is acidic or alkaline with a metal concentration of 1mg/m*l*.

However, one year or longer use is not recommended.

In storing any standard solution, avoid direct sunlight and store it in a cool place.

## 3.2 Standard solution for calibration curve

The standard solution for a calibration curve can be used for analysis after it has been diluted.

For flame atomic absorption, it should be a 1/1000 dilution (ppm). For electro-thermal (flameless) atomic absorption, it should be a 1/100,000 to a 1/1,000,000 dilution.

When the stock standard is diluted with water only, precipitation and absorption are susceptible and concentration values drop with many elements. Therefore, the solution of the same acid or alkali of 0.1M concentration is used to prepare the standard solution for the calibration curve.

The standard solution for calibration will easily change with long use, and it is recommended to prepare it fresh for every use.

Fig. 3.1 shows an example of change on standing when the standard solution diluted with water only is used for Fe measurement.

Fe stock standard has a concentration of 1000 ppm and hydrochloric acid concentration is 0.1M. It was diluted with water to obtain 0.5, 1.0, 1.5 and 2.0 ppm.

Measurement was conducted immediately after the stock standard was prepared, and was conducted every hour up to five hours. The 0.5 ppm solution showed a concentration drop after one hour and even the 2.0 ppm solution showed a concentration drop after three hours. After 5 hours, the 0.5 and 1.0 ppm solution showed a concentration drop of almost half the values.

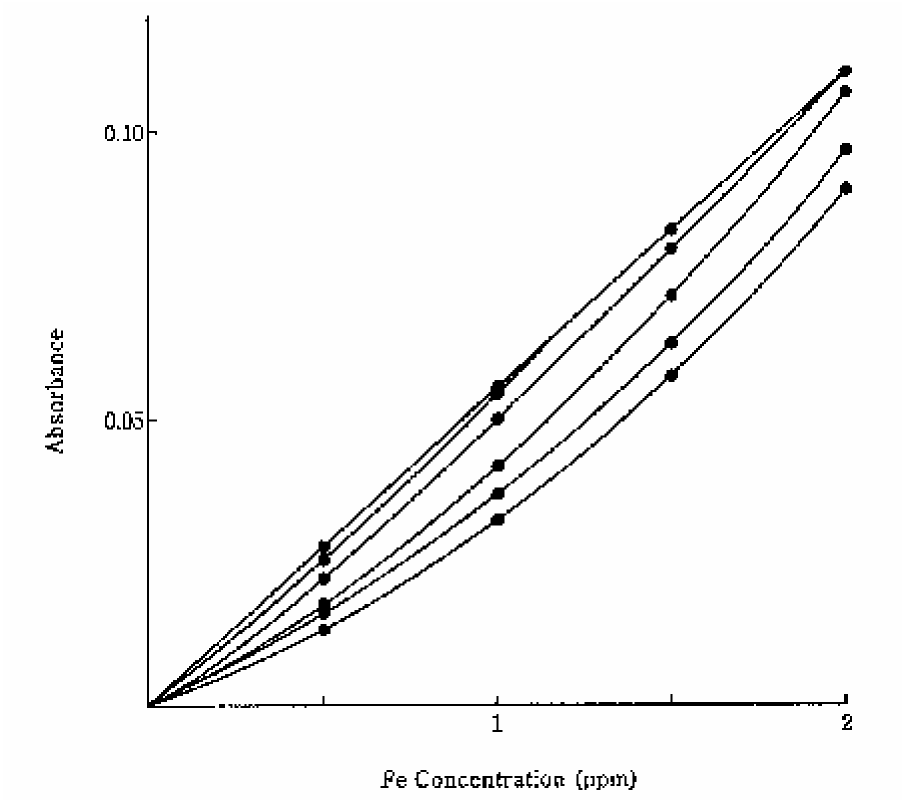


**Fig. 3.1 Change on standing of Fe standard sample**

## 3.3 Standard solution preparation method

### 1. Ag (Silver)

1.0mg Ag/m*l* Standard material: Silver nitrate ($AgNO_3$)

Preparation method of solution : 1.575g of silver nitrate dried at 110°C dissolved with nitric acid (0.1N) and is diluted with nitric acid (0.1N) to 1000m*l* accurately.

### 2. A*l* (Aluminum)

1.0mg A*l*/m*l* Standard material: Metal aluminum 99.9% up

Preparation method of solution : 1,000g of metal aluminum is heated and dissolved with hydrochloric acid (1+1) 50m*l* and is diluted with water to 1000m*l* accurately after it has cooled. (Hydrochloric acid concentration is changed to about 1N.)

### 3. As (Arsenic)

1.0mg As/m*l* Standard material: Arsenic (III) trioxide 99.9% up

Preparation method of solution : Arsenic (III) trioxide is heated at 105°C for about two hours and is cooled with the desiccator. Its 1.320g is dissolved in the smallest possible sodium hydroxide solution (1N) and is diluted with water to 1000m*l* accurately.

### 4. Au (Gold)

1.0mg Au/m*l* Standard material: Gold

Preparation method of solution : 0.100g of high purity gold is dissolved in several m*l* of aqua regia and vaporized to dryness on water bath. Then, 1 m*l* of hydrochloric acid is added and vaporized to dryness. It is dissolved in hydrochloric acid and water and diluted with water to 100m*l* accurately. Hydrochloric acid concentration is set at 1N.

### 5. B (Boron)

1.0mg B/m*l* Standard material: Boric acid ($H_3BO_3$)

Preparation method of solution : 5.715g of pure boric acid is dissolved in water and is diluted to 1000m*l*.

### 6. Be (Beryllium)

1.0mg Be/m*l* Standard material: Metal beryllium 99.9% up

Preparation method of solution : 0.100g of metal beryllium is heated and dissolved with hydrochloric acid (1+1) 10m*l* and is diluted with water to 100m*l* after it has cooled. Hydrochloric acid concentration is set at 1N.

### 7. Bi (Bismuth)

1.0mg Bi/m*l* Standard material: Metal bismuth 99.9% up

Preparation method of solution : 0.100g of metal bismuth is heated and dissolved with nitric acid (1+1) 20ml and is diluted to 100ml accurately after it has cooled.

### 8. Ca (Calcium)

1.0mg Ca/m*l* Standard material: Calcium carbonate ($CaCO_3$)

Preparation method of solution : 0.2497g of calcium carbonate dried at 110$^{o}$C for about one hour is dissolved with hydrochloric acid (1+1) 5m*l* and is diluted with water to 100m*l* accurately.

### 9. Cd (Cadmium)

1.0mg Cd/m*l* Standard material: Metal cadmium 99.9% up

Preparation method of solution : 1,000g of metal cadmium is heated and dissolved with nitric acid (1+1) 30 m*l* and is diluted with water to 1000m*l* accurately after it has cooled.

### 10. Co (Cobalt)

1.0mg Co/m*l* Standard material: Metal cobalt 9.9% up

Preparation method of solution : 1.000g of metal cobalt is heated and dissolved with nitric acid (1+1) 30 m and is diluted with water to 1000m*l* accurately after it has cooled.

### 11. Cr (Chromium)

1.0mg Cr/m*l* Standard material: Metal chromium 99.9% up

Preparation method of solution : 1.000g of metal chromium is heated and dissolved with 20m*l* of aqua regia and is diluted with water to 1000m*l* accurately after it has cooled.

### 12. Cs (Cesium)

1.0mg Cs/m*l* Standard material: Cesium chloride (CsCl)

Preparation method of solution : 1.267g of cesium chloride is dissolved in water and is diluted to 1000m*l* accurately with water after hydrochloric acid is added.

### 13. Cu (Copper)

1.0mg Cu/m*l* Standard material: Metal copper 99.9% up

Preparation method of solution : 1.000g of metal copper is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted to 1000m*l* accurately with 50m*l* if nitric acid (1+1) and water after it has cooled.

### 14. Fe (Iron)

1.0mg Fe/m*l* Standard material: Pure iron 99.9% up

Preparation method of solution : 1.000g of pure iron is heated and dissolved with 20m*l* of aqua regia and is diluted to 1000m*l* accurately after it has cooled.

### 15. Ge (Germanium)

1.0mg Ge/m*l* Standard material: Germanium oxide ($GeO_2$)

Preparation method of solution : 1g of sodium hydroxide and 20m*l* of water are added to 1.439g of germanium oxide, heated, and dissolved. It is diluted to 1000m*l* accurately with water after it has cooled.

### 16. Hg (Mercury)

1.0mg Hg/m*l* Standard material: Mercury chloride ($HgCl_2$)

Preparation method of solution : 1.354g of mercury chloride is dissolved in water and is diluted to 1000m*l* accurately with water.

### 17. K (Potassium)

1.0mg K/m*l* Standard material: Potassium chloride (KCl)

Preparation method of solution : Potassium chloride is heated at 600°C for about one hour and is cooled in the desiccator. Its 1.907g is dissolved in water and diluted to 1000m*l* accurately with water after hydrochloric acid is added. Hydrochloric acid concentration is set at 0.1N.

### 18. Li (Lithium)

1.0mg Li/m*l* Standard material: Lithium chloride (LiCl)

Preparation method of solution : 0.611g of lithium chloride is dissolved in water and diluted with water to 1000m*l* accurately after hydrochloric acid is added. Hydrochloric acid concentration is set at 0.1N.

### 19. Mg (Magnesium)

1.0mg Mg/m*l* Standard material: Metal magnesium 99.9% up

Preparation method of solution : 1.000g of metal magnesium is heated and dissolved with hydrochloric acid (1+5) 60m*l* and is diluted with water to 1000m*l* accurately after it has cooled.

### 20. Mn (Manganese)

1.0mg Mn/m*l* Standard material: Metal manganese 99.9% up

Preparation method of solution : 1.000g of metal manganese is heated and dissolved with 20m*l* of aqua regia and is diluted to 1000m*l* accurately after it has cooled.

### 21. Mo (Molybdenum)

1.0mg Mo/m*l* Standard material: Metal molybdenum 99.9% up

Preparation method of solution : 1.000g of metal molybdenum is heated and dissolved with hydrochloric acid (1+1) 30m*l* and a small quantity of nitric and is diluted to 1000m*l* accurately with water after it has cooled.

### 22. Na (Sodium)

1.0mg Na/m*l* Standard material: Sodium chloride (NaCl)

Preparation method of solution : Sodium chloride is heated at $600^{\circ}$C for about one hour and is cooled in the desiccator. Its 2.542g is dissolved in water and is diluted with water to 1000m*l* accurately after hydrochloric acid is added. Hydrochloric acid concentration is set at 0.1N.

### 23. Ni (Nickel)

1.0mg Ni/m*l* Standard material: Metal nickel 99.9% up

Preparation method of solution : 1.000g of metal nickel is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted to 1000m*l* accurately with water.

### 24. Pb (Lead)

1.0mg Pb/m*l* Standard material: Metal lead 99.9% up

Preparation method of solution : 1.000g of metal lead is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted with water to 1000m*l* accurately.

### 25. Pd (Palladium)

1.0mg Pd/m*l* Standard material: Metal palladium 99.9% up

Preparation method of solution : 1.000g of metal palladium is heated and dissolved with 30m*l* of aqua regia and is vaporized to dryness on a water bath.

Hydrochloric acid is added and it is vaporized to dryness again. Hydrochloric acid and water are added to dissolve it.

It is then diluted with water to 1000m*l* accurately. Hydrochloric acid concentration is set at 0.1N.

### 26. Pt (Platinum)

1.0mg Pt/m*l* Standard material: Platinum 99.9% up

Preparation method of solution : 0.001g of platinum is heated and dissolved with 20m*l* of aqua regia and vaporized to dryness on a water bath.

It is then dissolved with hydrochloric acid and diluted with water to 100 m*l* accurately. Hydrochloric acid concentration is set at 0.1N.

### 27. Sb (Antimony)

| | | |
|---|---|---|
| 1.0mg Sb/m*l* | | Standard material: Metal antimony 99.9% up |
| Preparation method of solution | : | 0.001g of metal antimony is heated and dissolved with 20m*l* of aqua regia and is diluted with hydrochloric acid (1+1) to 100m*l* after it has cooled. |

### 28. Si (Silicon)

| | | |
|---|---|---|
| 1.0mg Si/m*l* | | Standard material: Silicon dioxide ($SiO_2$) |
| Preparation method of solution | : | Silicon dioxide is heated at 700 to 800°C for one hour and cooled in the desiccator. Its 0.214g is put in a crucible, is dissolved by mixing 2.0h of sodium carbonate anhydrous, and is diluted with water to 100m*l* accurately. |

### 29. Sn (Tin)

| | | |
|---|---|---|
| 1.0mg Sn/m*l* | | Standard material: Metal tin 99.9% up |
| Preparation method of solution | : | 0.500g of metal tin is added to 50m*l* of hydrochloric acid. Then heated and dissolved at 50 to 80°C. After it has cooled, it is added to 200m*l* or hydrochloric acid and diluted with water to 500m*l* accurately. |

### 30. Sr (Strontium)

| | | |
|---|---|---|
| 1.0mg Sr/m*l* | | Standard material: Strontium carbonate ($SrCO_3$) |
| Preparation method of solution | : | 1.685g of strontium carbonate is dissolved with hydrochloric acid.<br>It is heated to remove carbon dioxide and is diluted to 1000m*l* accurately with water after it has cooled. |

### 31. Ti (Titanium)

| | | |
|---|---|---|
| 1.0mg Ti/m*l* | | Standard material: Metal titanium 99.9% up |
| Preparation method of solution | : | 0.500g of metal titanium is heated and dissolved with hydrochloric acid (1+1) 100m*l* and is diluted with hydrochloric acid (1+2) to 500m*l* accurately after it has cooled. |

### 32. Tl (Thallium)

| | | |
|---|---|---|
| 1.0mg Tl/m*l* | | Standard material: Metal thallium 99.9% up |
| Preparation method of solution | : | 1.000g of metal thallium is heated and dissolved with nitric acid (1+1) 20m*l* and is diluted with water to 1000m*l* accurately after it has cooled. |

### 33. V (Vanadium)

| | | |
|---|---|---|
| 1.0mg V/m*l* | | Standard material: Metal vanadium 99.9% up |
| Preparation method of solution | : | 1.000g of metal vanadium is heated and dissolved with 30m*l* of aqua regia and is concentrated to near dryness.<br>It is added to 20m*l* of hydrochloric acid and is diluted with water to 1000m*l* accurately after it has cooled. |

### 34. Zn (Zinc)

| | | |
|---|---|---|
| 1.0mg Zn/m*l* | | Standard material: Metal zinc 99.9% up |
| Preparation method of solution | : | 1.000g of metal zinc is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted with water to 1000m*l* accurately after it has cooled. |

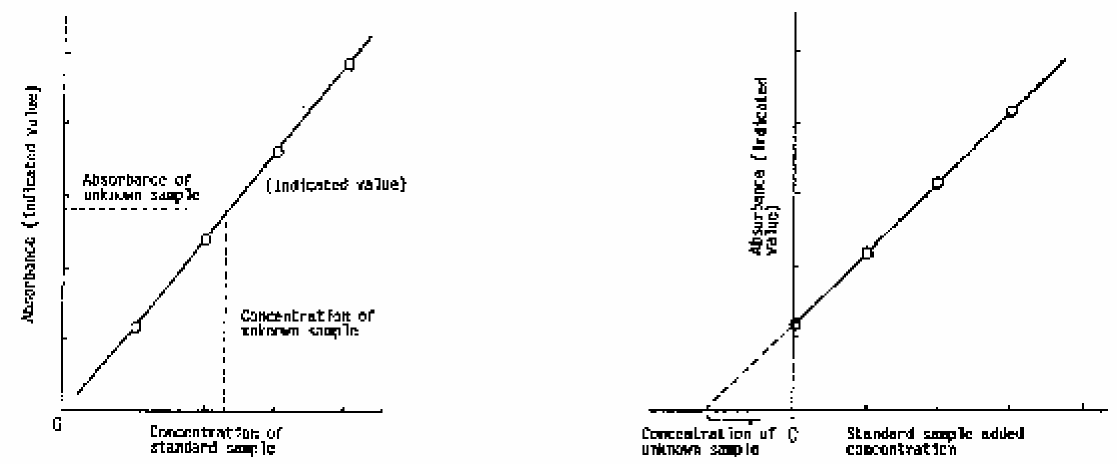
## 4. Preparation of calibration curve and determination method

Atomic absorption spectrometry determines the sample by using the fact that sample concentrations are proportional to light absorbance's in the atomization stage. (1) Calibration curve method and (2) Standard addition method are available as the determination method.

The calibration curve in atomic absorption spectrometry generally shows good linearity in the low concentration area, but is curved by various causes in the high concentration area to cause errors. Therefore, it is recommended to use the good linearity concentration area.

### 4.1 Calibration curve method

Several sample solutions of known concentration (Three or more solutions of different concentrations) are measured in advance, the calibration curve of concentration versus absorption is prepared as shown in Fig. 4.1 (1), and absorbance of unknown samples is measured to obtain the concentration of the target element from the calibration curve. If there is a difference in composition between the standard sample and unknown sample solution, an error may be given in the measured value. Therefore, it is recommended that the compositions of the standard sample and the unknown sample solution are similar. Concentration of the standard sample solution is prepared so that the concentration of the unknown sample solution is an inserted value.


(1) Calibration curve method

(2) Standard addition method

Fig. 4.1 Calibration curve

### 4.2 Standard addition method

Several unknown sample solutions (four or more) of a like quantity and standard sample solutions of known different concentrations are added. Absorbances of these series of samples are measured. The calibration curve of absorbance versus standard sample solution concentration is prepared as shown in Fig. 4.1 (2). It is extrapolated and the length of the axis of the abscissas from the point intersecting with the axis of the abscissas (concentration axis) to the added concentration 0 is considered as concentration of the unknown sample.

Fig. 4.2 shows a preparation example of the sample solution in the standard addition method. Four 100m*l* measuring flasks are prepared and 10m*l* of the unknown sample of Mg concentration of 100 x ppm is put in each of the above flasks. 0, 10, 20 and 30m*l* of Mg standard solution of concentration 1.0ppm are put in each of the above flasks.

Then, solvent is added so that the total quantity is 100m*l*.

Samples of Mg concentration x, x+0.1, x+0.2, x+0.3 ppm are now available. They are measured and the calibration curve is prepared as shown in Fig. 4.2 (2) to obtain Mg concentration of X ppm. If this value is multiplied ten times, Mg concentration in the unknown sample can be obtained.

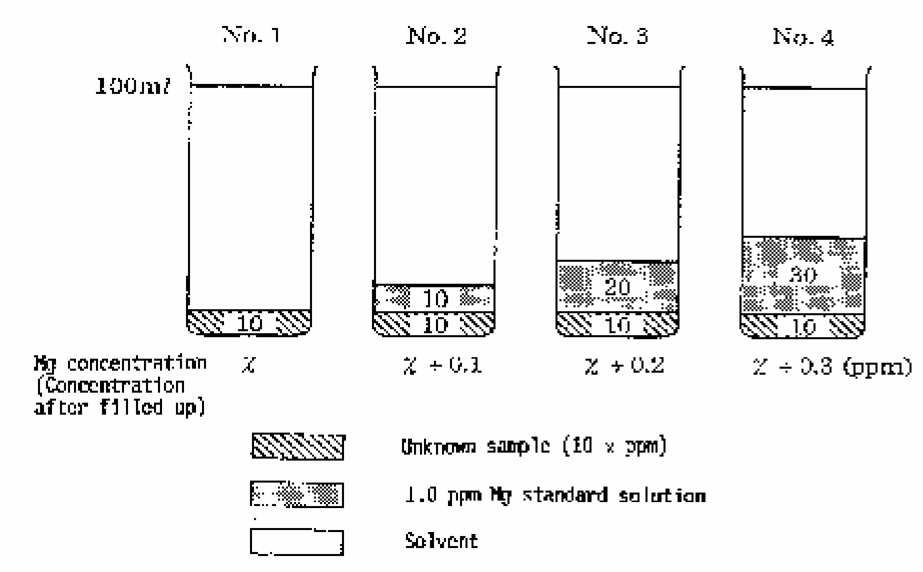


**Fig. 4.2 Example preparation of standard solution in standard addition method**

The advantage of this method is that it decreases analysis errors caused by various interferences based on differences in composition. Because the composition of the calibration curve is close to that of the sample, the calibration curve shows good linearity even in the low concentration area and passes the zero point. Otherwise, an error occurs.

### 4.3 Concentration of calibration curve

The range where the calibration curve shows linearity in atomic absorption spectrometry is generally said to be up to absorbance 0.5 and it is desirable to set the calibration curve at absorption 0.3 or less with some margin given. In the meantime, absorbance sensitivity is shown by 1% absorption value (0.0044 Abs.) or detection limit value in the atomic absorption spectrometry. 1% absorption value is the concentration of the sample, which gives absorbance 0.0044, and the detection limit value is the concentration of the sample, which gives a signal having amplitude twice as much as the noise width.

Because 1% absorbance sensitivity corresponds to 0.004 Abs. when the concentration of the calibration curve is set, the sample concentration with its lower limit of the calibration line being ten-fold concentration of 1% absorption value and with its upper limit being 70 to 80-fold concentration and showing 0.004 to 0.3 absorbance is considered as the optimum concentration range of the calibration curve. If Cd is taken as an example, the concentration range of the calibration curve is 0.12 to 0.96 ppm, because 1% absorption value in flame atomic absorption method is 0.012 ppm as shown in Table 4.1.

When the concentration range of the calibration curve is determined from the detection limit value, the concentration range of the calibration curve is about 1000-fold the detection limit value, because the detection limit value is 1/10 to 1/20 of 1% absorption value.

When the concentration of the unknown sample is below the concentration range of the calibration curve set by this method, the concentration for determination is to 1% absorption value in flame atomic absorption method It is five times that of the 1% absorption value in the electro thermal atomic absorption method, although accuracy  becomes slightly deteriorated. When the concentration of the unknown sample is above the set concentration range, the burner angle is adjusted to lower sensitivity in the flame atomic absorption method. Fig. 4.3 shows the relation between the burner angle and sensitivity. If the burner angle is tilted by $90^{o}$, the sensitivity drops to 1/20 and determination can be made to 20-fold the concentration of X the standard condition.

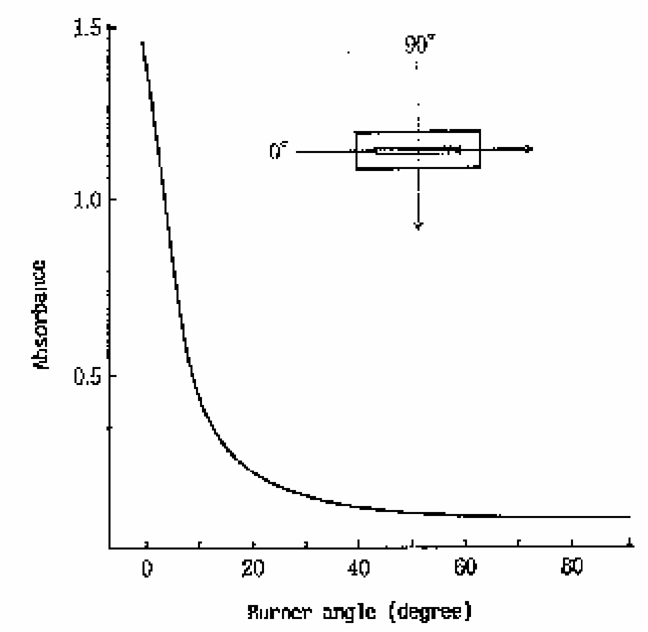


**Fig. 4.3  Relation between burner angle and sensitivity**

## Table 4.1 1% absorption value in the flame and electro thermal atomic absorption methods

| Element | Analysis line wavelerngth (nm) | Flame atomic absorption | | Electro-thermal atomic absorption | |
|---|---|---|---|---|---|
| | | Gas type | 1% absorption concentration (ppm) | 1% absorption concentration (ppb) Low | 1% absorption concentration (ppb) High |
| Ag | 328.1 | Air-$C_2H_2$ | 0.04 | | |
| Al | 309.3 | $N_2O$-$C_2H_2$ | 0.63 | 0.5 | 0.14 |
| As | 193.7 | Ar-$H_2$ | 0.4 | 1.0 | 0.22 |
| Au | 242.8 | Air-$C_2H_2$ | 0.2 | 0.48 | |
| B | 249.7 | $N_2O$-$C_2H_2$ | 12 | | |
| Ba | 553.5 | $N_2O$-$C_2H_2$ | 0.25 | | |
| Be | 234.9 | $N_2O$-$C_2H_2$ | 0.025 | | |
| Bi | 223.1 | Air-$C_2H_2$ | 0.25 | 0.55 | |
| Ca(1) | 422.7 | Air-$C_2H_2$ | 0.06 | 0.06 | |
| Ca(2) | 422.7 | $N_2O$-$C_2H_2$ | 0.02 | | |
| Cd | 228.8 | Air-$C_2H_2$ | 0.012 | 0.02 | 0.005 |
| Co | 240.7 | Air-$C_2H_2$ | 0.06 | 0.28 | 0.07 |
| Cr | 357.9 | Air-$C_2H_2$ | 0.08 | 0.10 | 0.05 |
| Cs | 852.1 | Air-$C_2H_2$ | 0.03 | | |
| Cu | 324.7 | Air-$C_2H_2$ | 0.04 | 0.20 | 0.05 |
| Dy | 421.2 | $N_2O$-$C_2H_2$ | 1.0 | | |
| Er | 400.8 | $N_2O$-$C_2H_2$ | 0.8 | | |
| Eu | 459.4 | $N_2O$-$C_2H_2$ | 0.5 | | |
| Fe | 248.3 | Air-$C_2H_2$ | 0.08 | 0.19 | 0.12 |
| Ga | 287.4 | Air-$C_2H_2$ | 1.3 | | |
| Gd | 368.4 | $N_2O$-$C_2H_2$ | 30 | | |
| Ge | 265.1 | $N_2O$-$C_2H_2$ | 1.7 | | |
| Hf | 307.3 | $N_2O$-$C_2H_2$ | 16 | | |
| Hg | 253.7 | | 0.14 | | |
| Ho | 410.4 | $N_2O$-$C_2H_2$ | 1.2 | | |
| Ir | 208.8 | Air-$C_2H_2$ | 1.4 | | |
| K | 766.5 | Air-$C_2H_2$ | 0.012 | 0.03 | |
| La | 550.1 | $N_2O$-$C_2H_2$ | 70 | | |
| Li | 670.8 | Air-$C_2H_2$ | 0.03 | | |
| Lu | 360.0 | $N_2O$-$C_2H_2$ | 12 | | |
| Mg | 285.2 | Air-$C_2H_2$ | 0.0035 | 0.02 | |
| Mn | 279.5 | Air-$C_2H_2$ | 0.028 | 0.15 | 0.02 |
| Mo | 313.3 | $N_2O$-$C_2H_2$ | 0.5 | | 0.5 |
| Na | 589.0 | Air-$C_2H_2$ | 0.005 | 0.02 | 0.004 |
| Nb | 334.9 | $N_2O$-$C_2H_2$ | 30 | | |
| Ni | 232.0 | Air-$C_2H_2$ | 0.08 | 0.40 | 0.16 |
| Os | 290.9 | $N_2O$-$C_2H_2$ | 1.5 | | |
| Pb(1) | 217.0 | Air-$C_2H_2$ | 0.1 | | |
| Pb(2) | 283.3 | Air-$C_2H_2$ | 0.25 | 0.29 | 0.13 |

| Element | Analysis line wavelerngth (nm) | Flame atomic absorption |  | Electro-thermal atomic absorption |  |
|---|---|---|---|---|---|
|  |  | Gas type | 1% absorption concentration (ppm) | 1% absorption concentration (ppb) Low | 1% absorption concentration (ppb) High |
| Pd | 247.6 | Air-$C_2H_2$ | 0.09 |  |  |
| Pr | 495.1 | $N_2O$-$C_2H_2$ | 30 |  |  |
| Pt | 265.9 | Air-$C_2H_2$ | 1.3 | 0.35 |  |
| Rb | 780.0 | Air-$C_2H_2$ | 0.06 |  |  |
| Re | 346.0 | $N_2O$-$C_2H_2$ | 12 |  |  |
| Ru | 349.9 | Air-$C_2H_2$ | 0.6 |  |  |
| Sb | 217.6 | Air-$C_2H_2$ | 0.33 | 1.6 | 0.25 |
| Sc | 391.2 | $N_2O$-$C_2H_2$ | 0.5 |  |  |
| Se | 196.0 | Ar-$H_2$ | 0.5 | 0.7 | 0.28 |
| Si | 251.6 | $N_2O$-$C_2H_2$ | 1.3 |  | 0.57 |
| Sm | 429.7 | $N_2O$-$C_2H_2$ | 15 |  |  |
| Sn(1) | 224.6 | Air-$C_2H_2$ | 2.0 |  | 2.0 |
| Sn(2) | 286.3 | Air-$C_2H_2$ | 5.0 | 5.5 |  |
| Sn(3) | 224.6 | $N_2O$-$C_2H_2$ | 0.8 |  |  |
| Sn(4) | 286.3 | $N_2O$-$C_2H_2$ | 2.0 |  |  |
| Sr | 460.7 | Air-$C_2H_2$ | 0.06 |  |  |
| Ta | 271.5 | $N_2O$-$C_2H_2$ | 15 |  |  |
| Tb | 432.6 | $N_2O$-$C_2H_2$ | 12 |  |  |
| Te | 214.3 | Air-$C_2H_2$ | 0.3 | 2.1 |  |
| Ti | 364.3 | $N_2O$-$C_2H_2$ | 1.8 | 2.1 |  |
| Tl | 276.8 | Air-$C_2H_2$ | 0.3 |  |  |
| V | 318.4 | $N_2O$-$C_2H_2$ | 1.0 | 1.3 |  |
| W | 255.1 | $N_2O$-$C_2H_2$ | 8.0 |  |  |
| Y | 410.2 | $N_2O$-$C_2H_2$ | 3.0 |  |  |
| Yb | 398.8 | $N_2O$-$C_2H_2$ | 0.1 |  |  |
| Zn | 213.9 | Air-$C_2H_2$ | 0.011 | 0.03 |  |
| Zr | 360.1 | $N_2O$-$C_2H_2$ | 15 |  |  |
| As(H) | 193.7 | Air-$C_2H_2$ | 0.06 |  |  |
| Bi(H) | 223.1 | Air-$C_2H_2$ |  |  |  |
| Sb(H) | 217.6 | Air-$C_2H_2$ | 0.12 |  |  |
| Se(H) | 196.0 | Air-$C_2H_2$ | 0.25 |  |  |
| Sn(H) | 286.3 | Air-$C_2H_2$ |  |  |  |
| Te(H) | 214.3 | Air-$C_2H_2$ |  |  |  |

## 5. Interference in atomic absorption spectrophotometer

Interferences in atomic absorption spectrometry are generally classified into Spectrophotometric interferences, physical interferences, and chemical interferences.

Spectrophotometric interference is based on equipment and flame properties. It occurs when the spectral line used for analysis cannot be separated completely from other nearby lines, or when the spectral line used for analysis is absorbed by substances other than the atomic vapor of the target element produced in the flame. Physical interference occurs due to an error in the supply of the sample into the flame by influences of physical condition such as viscosity of the sample solution and/or surface tension.

Chemical interference is peculiar to the sample and the element it occurs when atoms are ionized in the flame, or when atoms act on coexistent substances to produce hard-to-dissociate (break) compounds. The number of atoms in ground state, which contribute to absorption, decreases.

### 5.1 Spectrophotometric interference and its correction method

Spectrophotometric interference is caused by an atomic beam or molecular absorption. Interference by an atomic beam is caused when the spectral line used for measurement and other nearby spectral lines overlap each other.

Interference is shown if the other elements spectrum component is included when the target element is measured like Eu3247 (530A) for Cu3247 (540A) or V2506 (905A) for Si2506 (899A). Interference of this type is not general and can be avoided by selecting the analysis line showing no interference. Obstruction of Fe2138 (589A) from Zn2138 (56A) appears in the case of determination, where Fe coexists in a large quantity like Zn in steel. A wrong analysis value is obtained if spectro interference is neglected.

Interference by molecular absorbance is light absorption and scattering by molecules, which are not atomized.

Light scattering occurs when fine solid particles pass the light beam. The most typical example of this phenomenon is seen when the sample is heated and smoke is emitted in the electro-thermal atomic absorption. Scattering peak by this smoke increases as wavelength decreases. It often becomes an issue in measurement of the element with wavelength of 250 mm or less. The heating condition is adjusted, in the electro-thermal atomic absorption, to expel such smoke in the ashing stage and prevent the smoke in the atomizing stage.

Separation of the scattering peak and the atomic absorption peak becomes imperfect, and an error is given in measurement, when smoke generating temperature is close to the atomizing temperature of the target element. Molecular absorption occurs when NaCl or other salts in the sample evaporate in the molecular form. Absorption of salt molecules occurs in the wide wavelength range of the ultraviolet region. (Refer to Fig. 5.1)

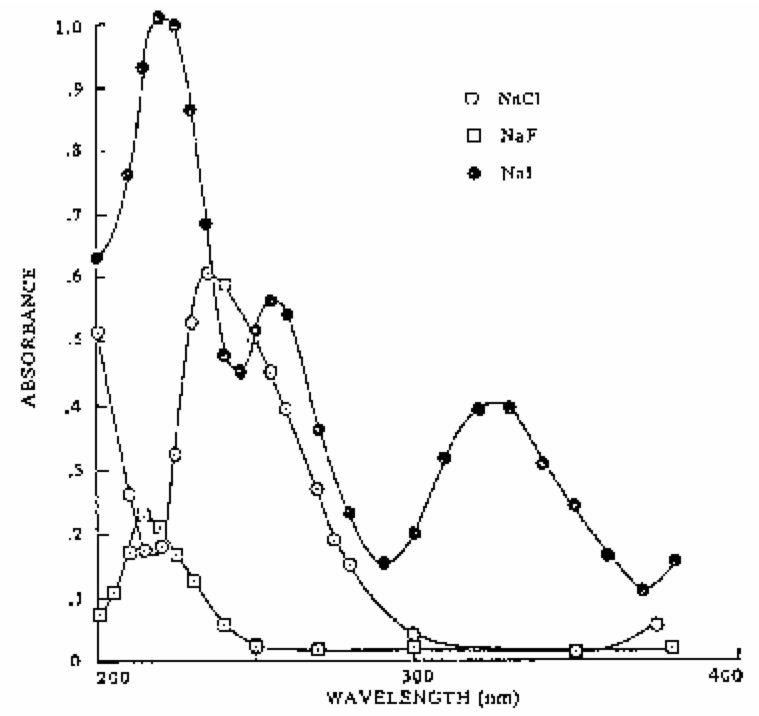


**Fig. 5.1 Molecular absorption by sodium compound**

In measurement of the element having the analysis line in the wavelength range shown in Fig. 5.1, the sum of atomic absorption and molecular absorption is measured to give a big plus error. Such molecular absorption becomes an issue in respect to the percent salt concentration in the flame analysis, and becomes an issue in respect to several hundred ppm salt concentration.

The molecular absorbance is called the background absorbance, and the sum of atomic absorbance and background absorbance is measured by light from the hollow cathode lamp source. If background absorption can only be measured by some means, atomic absorption can only be obtained by doing subtraction of both measured values.

Background absorption can be corrected by the following methods.

**Method by using nearby line**

At the wavelength slightly shifted from the analysis line of the target element, background absorption occurs, and atomic absorption does not. Therefore, if another hollow cathode lamp, which gives a nearby spectral line within ±5nm from the wavelength of the target element, only background absorption can be measured. This is the method using the nearby line.

A hollow cathode lamp, which gives strong light, is not always obtained within ±5nm. Even if it is obtained, there is the limitation that atomic absorption cannot occur at the wavelength. Such being the case, it cannot be an accurate background correction method. The method using a continuous light source, as described below, is used as the standard background correction method. Because it has no such limitation, a highly accurate correction can be made.

## Method using a continuous light source

If a light source, such as a deuterium lamp, is continuously giving off light in the wavelength range of 190 to 430 nm, an accurate background correction can be made.

When the wavelength of the spectroscope is set at the wavelength of the target element, the wide wavelength band can be observed in the light of the deuterium lamp.

As mentioned before, molecular absorption occurs in a wide wavelength range, and absorption occurs within this region. Also, an apparent decrease in the light intensity is observed. The target atom absorbs the light in the center of the wavelength only, and no absorption at a distance of 1/100 angstrom or more. Due to the intensity of the deuterium lamp, the greater part of the light observed is not absorbed.

The above shows that only molecular absorption (background absorption) can be measured if the deuterium lamp is used. Thus, atomic absorption can only be measured if subtraction is done from the absorption of the hollow cathode lamp (sum of atomic absorption and background absorption).

## Method by self-reversal

Background correction by self-reversal method uses a hollow cathode lamp for self-reversal (200-38456-XX) and lights the lamp by supplying high current combined with low current.

A in Fig. 5.2 shows lamp current waveform and high current $I_H$ is set at 300 to 600mA and low current $I_L$ at 60mA or less. It lights the lamp at a frequency of 100 Hz.

The spectrum emitted by the lamp current $I_H$ becomes two peaks (self reverse) with the depressed center as shown in the upper left of B in Fig. 5.2. This is due to internal absorption by a great deal of atomic clouds scattered from the hollow cathode lamp, as the half-width spreads.

Because atomic absorption occurs in a narrow wavelength region of about $10^{-2}$ A from the center of the absorption center, the analysis line, which causes self-reversal, has no light in the absorption wavelength region. Also, atomic absorption hardly appears as shown in the upper right of B in Fig. 5.2.

Background absorption, including molecular absorption and scattering, occurs in the wide wavelength region. Satisfactory absorption appears even in the analysis line, which causes self-reversal. Most of the signals are measured in the lower left of C in Fig. 5.2.

The spectrum emitted by the lamp current $I_L$ becomes one spectral line a having half-width of about $10^{-2}$ A. Both atomic absorption and background absorption appear in the lower right of B in Fig. 5.2. Signals measured in this condition become atomic absorption and background absorption as shown in the lower left of B in Fig. 5.2.

Then, if the $I_H$ signal is subtracted from the $I_L$ signal, background absorption is corrected and only atomic absorption is measured. The features of this correction method are shown below.

(1) Background correction can be made over the whole range from 190 to 900nm. (2) Atomic absorption and background absorption can be measured by one hollow cathode lamp, and correction accuracy is very high. (3) Spectro interference caused by the analysis line of other element near the element.

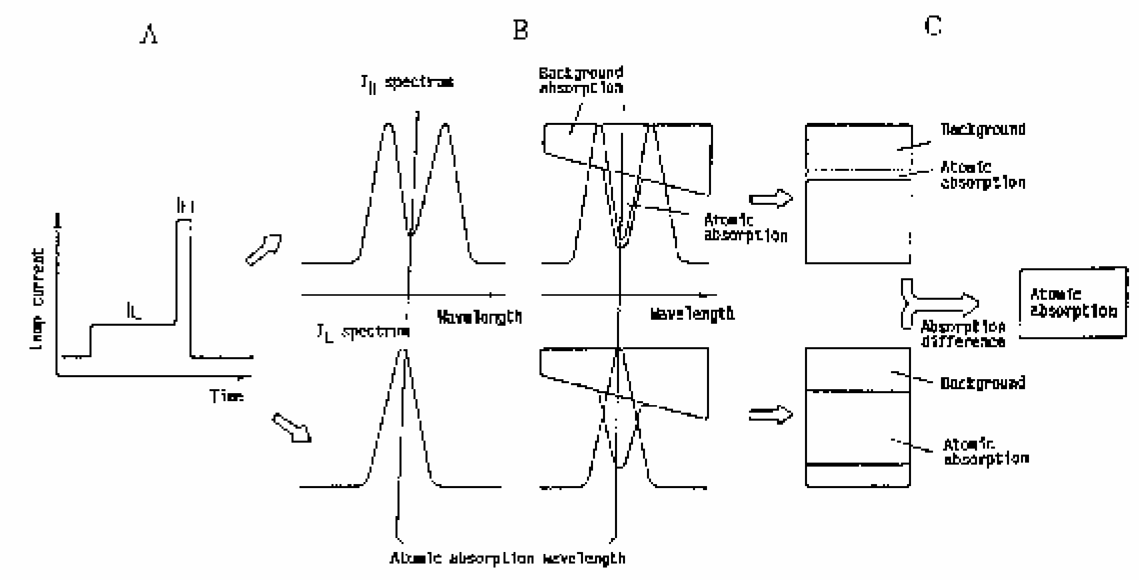


Fig. 5.2 Principle of background correction method by self-reversal

## 5.2 Physical interference

An error occurs in the analysis value because physical properties of the sample solution including viscosity and surface tension differ between that of the standard sample, and between samples. The difference in physical properties affects mist amount, the mist-generating rate, and the mist particle size in flame atomic absorption. The organic solvent effect uses the above phenomenon.

When the metal to be measured is dissolved in 4-methyl-2-pentanone, acetic acid-n-butyl, or other organic solvents, sensitivity rises two to three times that of its water solution.

In electro-thermal atomic absorption, differences in physical properties causes differences in sample diffusion or filtering in the graphite tube. When viscosity is high, some of the sample remains in the pipette or capillary resulting in analysis error.

The standard sample having the same composition as the sample is used for the correction. There are ways to extract and separate the target element, but the easiest method is to measure by the standard addition method.

### 5.3 Chemical interference and its correction method

The sample introduced into the flame becomes free atoms by the heat, but part of them may be ionized.

Because atomic absorption measures the quantity of free atoms, when ionization occurs (a negative interference), it causes a decrease in the absorbance. This is called ionization interference. The degree of ionization generally increases as the flame temperature increases, and the number of ionized metals increases. Ca, Sr, Ba, Rb, Li, Na, K, Cs and other metals which have 6.1eV or lower ionization potential, ionize at the air-acetylene flame temperature.

To check this interference, Cs, Rb and K, which are easy-to-ionize metals, are added to the sample and standard sample until its effect comes to a certain level.

Some of the sample introduced in the flame reacts on other particle types in the flame to produce a hard-to-dissociate compound or the salt produced in the solution becomes a hard-to-dissociate compound. A representative example of this is the interference when Mg, Ca or an alkaline earth metal is measured by the air-acetylene flame and there is interference as shown in Fig. 5.3 if Al exists. This happens because Mg and A*l* react in the flame and $MgO.Al_2O_3$ is produced.

Example of the latter is the interference of phosphoric acid against Mg, Ca or other alkaline earth metals. Phosphates in the solution produce hard-to-dissociate compounds in the air-acetylene flame. It should be noted that interferences by the production of hard-to-dissociate compounds easily occur if A*l*, Si, Ti, V, phosphoric acid, sulfuric acid, etc. coexist with the alkaline earth metal.

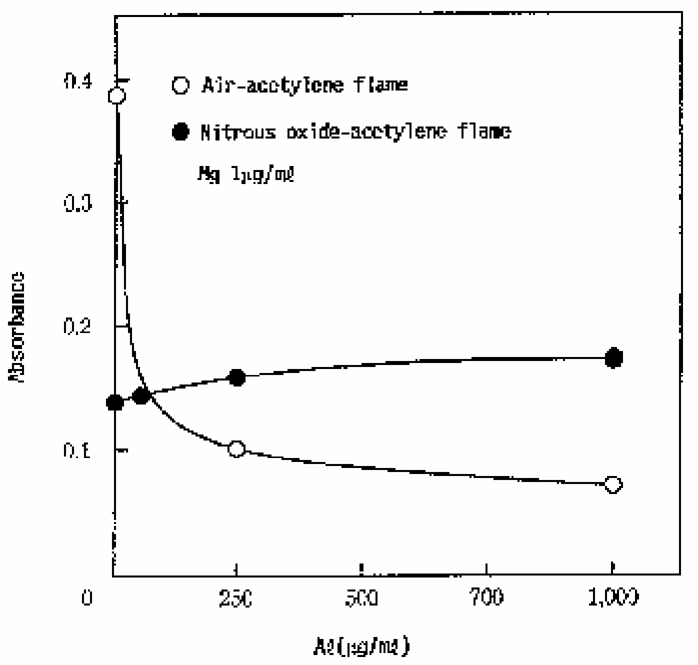


**Fig. 5.3 The influence of aluminum on magnesium**

**(Practice of atomic absorption spectrometry published by Nankodo)**

Because the sample is heated and atomization is done in the limited space of the graphite tube in the electro-thermal atomic absorption, chemical interference becomes much larger than in the flame atomic absorption. The interference process becomes complicated, and the reaction is different from that in the flame atomic absorption, because atomization is conducted in an argon environment.

To check these interferences, the following are done in the case of flame atomic absorption. (1) Removal of other elements spectrum, and extraction of target element by ion exchange and solvent extraction, (2) addition of excessive interference elements, (3) addition of interference inhibitors, (4) standard addition method, etc. To check interferences against the alkali earth metal described above, Sr, La, EDTA, or other chelating reagents are added. The use of nitrous oxide-acetylene flame is effective to check interferences by the production of a hard-to-dissociate compound, because the degree of interference is lower with the higher flame temperature.

To check interferences in the electro-thermal atomic absorption, the following are done in the same way as in the case of the flame atomic absorption. (1) Ion exchange and solvent extraction, (2) matrix accord or other techniques by the standard addition method, (3) matrix modifier is added.

Addition of the matrix modifier (a) raises absorption sensitivity of the measured element in the simple water solution, (b) the sensitivity which drops a lot is restored by the existence of coexistent matter, (c) or improved better than before, and addition concentration is generally at the several ppm level.

Table 3.1 shows representative combinations of the target element and matrix modifier.

**Table 5.1 Application examples of the matrix modifier method**
**(Fundamentals of atomic absorption spectrophotometer,**
**Textbook for Shimadzu course in atomic absorption spectrophotometer)**

| Target element | Matrix modifier | Remarks |
|---|---|---|
| Cd | Pd $(NO_3)_2 + NH_4NO_3$<br>$(NH_4)_2HPO_4 + HNO_3$<br>Mg $(NO_3)_2$<br>$(NH_4)H_2PO_4 + HNO_3$ or Mg $(NO_3)_2$ | ppb level OK with blood, serum and urine.<br>Addition of F', $SO_4$, $PO_4$ effective |
| Pb | Mg $(NO_3)_2$<br>La $(NO_3)_3$<br>Pd, Pt ( μg level) | Coexistence with $NaCl$, $KCl$, $MgCl_2$, etc. prevents $PbCl_2$ sublimation<br>Effective by alloying $HNO_3$ addition effective, high sensitivity attained by alloying |
| Hg | Sulfide + $HNO_3$<br>$HCl + H_2O_2$<br>$K_2Cr_2O_7 + Na_2S$<br>Au, Pt, Pd (μg level)<br>Se<br>Organic acid | Volatilization n prevention as HgS<br>For prevention of reduction vaporization<br>Volatilization prevention by amalgamation<br>Used for soil |

| | | |
|---|---|---|
| | (Succinic acid, tartaric acid) | |
| T2 | Pd, Pt, Ir | Alloying |
| | La (NO$_3$) | Alloying |
| Bi | Pb | MIBK extract |
| Sn | Mg (NO$_3$)$_2$, $(NH_4)_2HPO_4$ | Use with ascorbic acid to prevent interference |
| | La (NO$_3$)$_3$ | Effective by alloying |
| | $K_2$, $WO_4$, $K_2MO_4$ | Sensitivity improves remarkably but chloride interference exists |
| | $NH_4NO_3$, $(NH_4)_2C_2O_4$ | No chloride interference |
| Se | Mg (NO$_3$)$_2$ | Coexistence with Ni is effective (NiSe produced) |
| | Pd, Pt, Cu, A*l*, Ni | Particularly Pb good, PdSe produced |
| As | Pd best, Mo, Zr, Ba also good | Coexistence with Ni is effective |
| | La (NO$_3$)$_3$ | Production of $As_2O_6$ seems to be effective |
| Sb | Cu best, Ni, Pt also effective | Alloying |
| | La (NO$_3$)$_3$ | Alloying |
| T*l* | Pd+HC*l*O$_4$ | Coexistence with ascorbic acid is effective, Pd checks T*l*C*l* production |
| | La (NO$_3$)$_3$ | Alloying |
| In | Pd | Pd checks production of subliming InO |
| | La (NO$_3$)$_3$ | Alloying |
| Ga | Ni | Ni checks GaO production and avoids inorganic matter interference |
| Zn | Succinic acid, oxalic acid | MaC*l*$_2$ produces ZnC*l*$_2$ and sublimes. Organic acid check it |
| P | La (NO$_3$)$_3$ | Sensitivity improves by 6 times |
| Si, A*l*, Mn, Cu, Cd, Ba, Be, Cr | La (NO$_3$)$_3$ | Effective with alloying |

# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 3

### Measuring Conditions by Element of Flame Atomic Absorption Spectrophotometry

SHIMADZU CORPORATION

## Atomic Absorption Spectrophotometer Cookbook

## Section 3

## CONTENTS

# 6. Measuring Conditions by Element of Flame Atomic Absorption Spectrophotometer

## 6.1 Measuring concentration

The solution prepared based on the standard sample preparation method in the cookbook section 2 - 3 is used to make the calibration curve in the standard concentration range. Because absorbance is 0.044 to 0.3 in the cookbook section 2 - 4, the upper and lower limits of the calibration line are obtained from the above data to determine the practical measuring concentration range.

The measuring concentration range of an actual sample may differ from the data, due to a co-existent matter. Sensitivity of an organic solvent type sample is raised by two or three times.

To make a measurement of higher concentrations, the burner must be tilted (Cookbook Section 2 - 4.3) or another analysis line must be used. (Cookbook Section 1 - 2.1).

## 6.2 Measuring conditions

In the AA-6400 or the AA-6500, the analysis conditions stored can be used. Because there is a slight difference between instruments, it may be better to change the mixing ratio of oxidant and fuel gas in accordance with the cookbook (section 1 - 2.2). This allows data of high sensitivity and good repeatability to be obtained.

However, these conditions are for a water solution sample.

Therefore, oxidant flow, fuel gas flow, burner height and other conditions must be changed when an organic solvent type sample is measured. Refer to the operating instructions of the atomic absorption spectrophotometer for selection of the optimum conditions.

In the cases of calcium, lead, and tin as the target elements, two or more flame conditions and analysis wavelengths are indicated by an I, II, III, or IV.

## 6.3 Background correction method and interference

Concerning elements for which the self-reversal hollow cathode lamp is available, background correction is done by the $D_2$ lamp method and the self-reversal method. Their results are shown respectively as BGD-$D_2$ mode and BGC-SR mode. In case of BGC-SR, sensitivity drop occurs due to its principle reason. The BGC-$D_2$ is recommended as a rule when background correction is done.

But, in the case of a sample, which has the background absorption above 0.5Abs or has any spectral interface, or in the case its analysis line is in a longer wavelength range for which the $D_2$ lamp cannot be used, BGC-SR mode is desirable.

Data in this section shows information on interference.

In measuring an actual sample, confirmation of interference is necessary. Refer to the cookbook section 2 - 5 for interference in the atomic absorption method.

## 6.4 Measuring conditions by element

# Silver (Ag)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

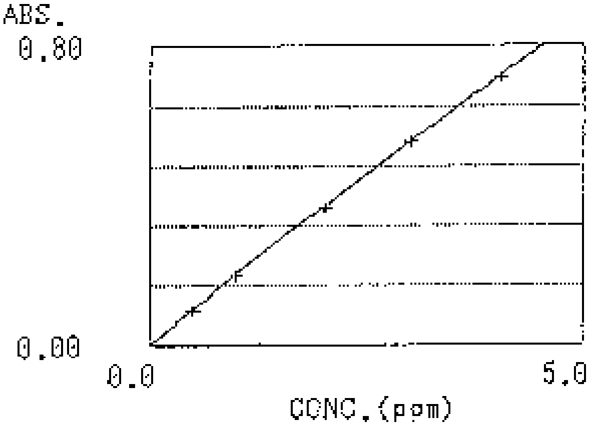
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/400 mA | Burner height | ; 7 mm |
| Wave length | ; 328.1 nm | ; 328.1 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.2 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.5000 | 0.0967 |
| 2 | 1.0000 | 0.1892 |
| 3 | 2.0000 | 0.3716 |
| 4 | 3.0000 | 0.5470 |
| 5 | 4.0000 | 0.7179 |

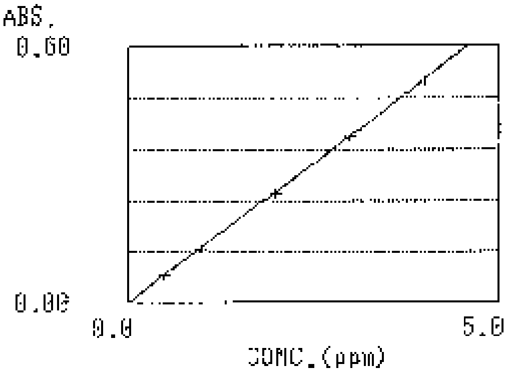


$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.1923, K2= –0.0032

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.5000 | 0.0645 |
| 2 | 1.0000 | 0.1297 |
| 3 | 2.0000 | 0.2596 |
| 4 | 3.0000 | 0.3903 |
| 5 | 4.0000 | 0.5215 |



$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.1293, K2= 0.0003

## Interference

Chemical interference hardly exists.

# Aluminum (A*l*)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

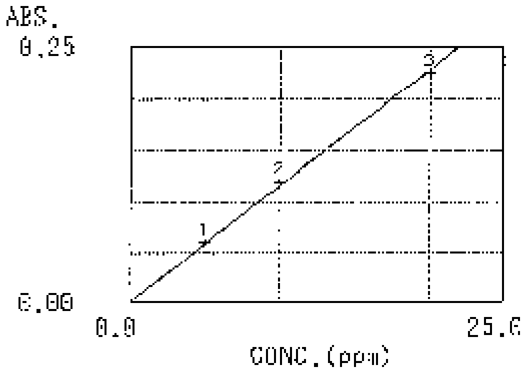
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/600 mA | Burner height | ; 17 mm |
| Wave length | ; 309.3 nm | ; 309.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 7.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 5.0000 | 0.0585 |
| 2 | 10.0000 | 0.1183 |
| 3 | 20.0000 | 0.2243 |

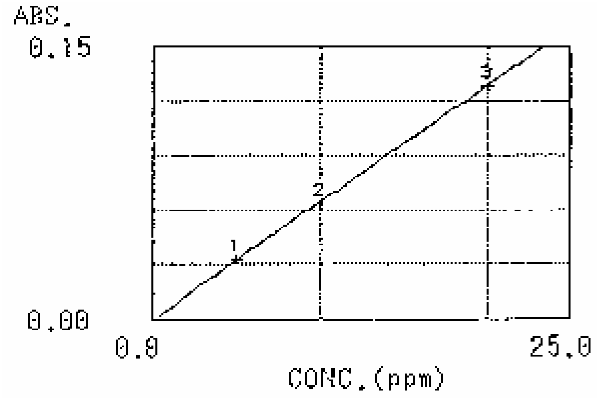


[ABS]=K1*[C]+K0

K0= 0.0000, K1= 0.0114

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 5.0000 | 0.0330 |
| 2 | 10.0000 | 0.0638 |
| 3 | 20.0000 | 0.1288 |



[ABS]=K1*[C]+K0

K0= 0.0000, K1= 0.0064

## Interference

A*l* is ionized 10 to 15% by $N_2O$-$C_2H_2$ flame. 0.1% lanthanum chloride or potassium is added to the standard or unknown sample as ionization restrainer.

About 10% positive interference is given if Ti and Fe coexist with A*l* in 10 to 50-fold concentration.

# Arsenic (As)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

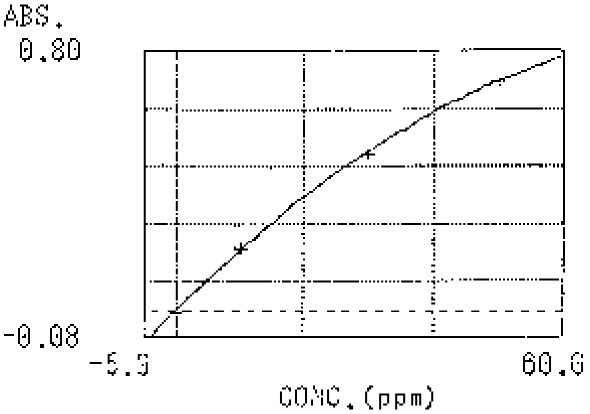
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 14 mA/0 mA | ; 14 mA/500 mA | Burner height | ; 15 mm |
| Wave length | ; 193.7 nm | ; 193.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 3.7 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

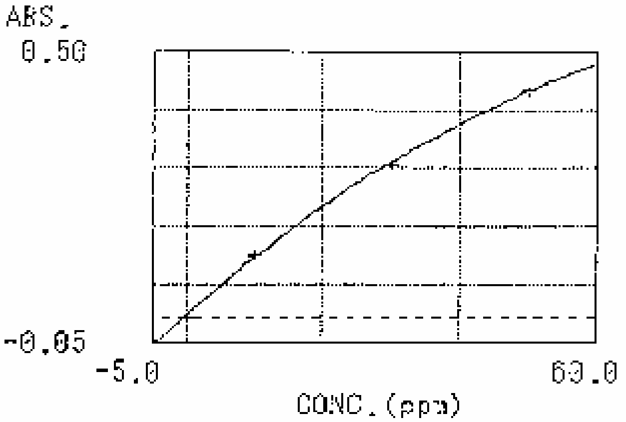
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>193.7nm |
|---|---|---|
| 1 | 0.0000 | –0.0042 |
| 2 | 10.0000 | 0.1965 |
| 3 | 30.0000 | 0.4890 |
| 4 | 50.0000 | 0.7096 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9996
K0= 0.0002, K1= 0.0200, K2= –0.0001

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>193.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0007 |
| 2 | 10.0000 | 0.1163 |
| 3 | 30.0000 | 0.2878 |
| 4 | 50.0000 | 0.4280 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9995
K0= 0.0036, K1= 0.0113, K2= –0.0000

## Interference

The greatest interference is diffusion and absorption by Air-$C_2H_2$ flame.

## Gold (Au)

The measuring method sending arsine gas directly to Ar-$H_2$ flame or heated quartz shell is recommended for sensitivity and interference.

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

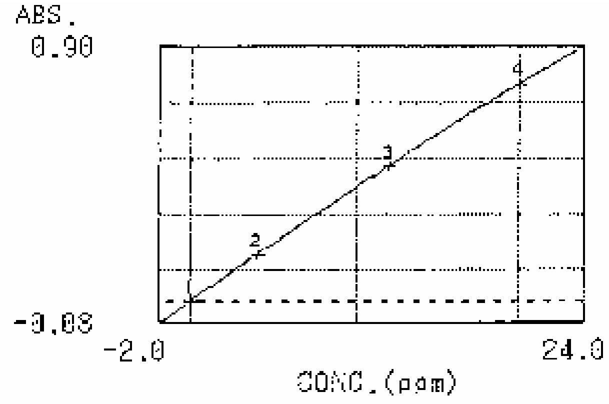
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 10 mA/400 mA | Burner height | ; 7 mm |
| Wave length | ; 242.8 nm | ; 242.8 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

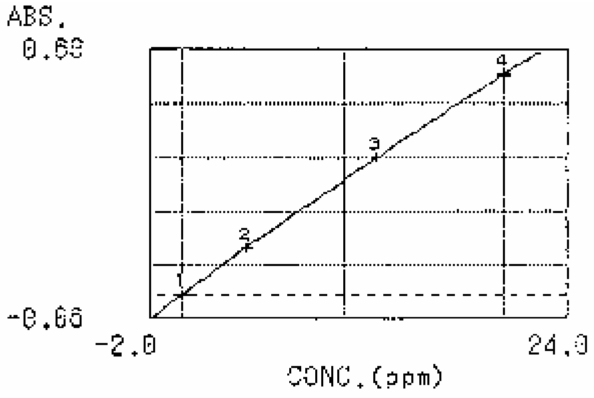
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | –0.0000 |
| 2 | 4.0000 | 0.1683 |
| 3 | 12.0000 | 0.4794 |
| 4 | 20.0000 | 0.7673 |



$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=1.0000$
K0= 0.0000, K1= 0.0424, K2= –0.0002

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | –0.0009 |
| 2 | 4.0000 | 0.1124 |
| 3 | 12.0000 | 0.3362 |
| 4 | 20.0000 | 0.5392 |



$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=1.0000$
K0= 0.0019, K1= 0.0296, K2= –0.0001

### Interference

If Fe, Cu and Ca coexist in large quantities, negative interference is given. However, chemical interference is generally small.

# Boron (B)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

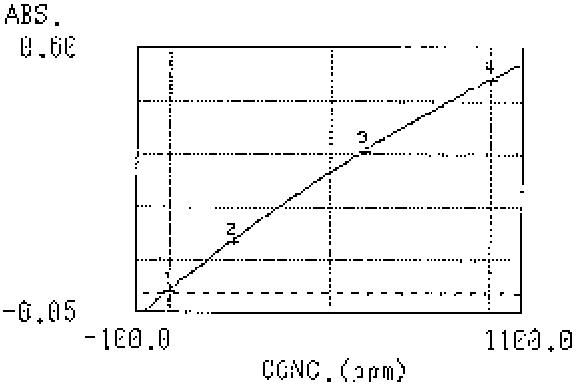
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 16 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 249.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 7.7 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>249.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0025 |
| 2 | 200.0000 | 0.1254 |
| 3 | 600.0000 | 0.3494 |
| 4 | 1000.0000 | 0.5219 |



$[ABS]=K2*[C]^2+K1*[C]+K0$ $r^2=0.9999$

K0= 0.0012, K1= 0.0007, K2= –0.0000

## Interference

If Na coexists in large quantities, positive interference is given. Interference can be decreased by changing the $C_2H_2$ quantity of the $N_2O$-$C_2H_2$ flame or burner height; but sensitivity also drops.

# Barium (Ba)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

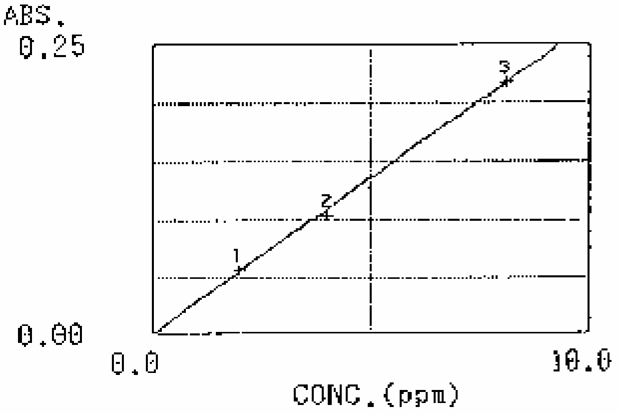
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 16 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 553.6 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 6.7 *l*/min |
| Lighting mode | ; HCL | Type of oxidant | ; $N_2O$ |

- Calibration curve in HCL mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>553.6nm |
|---|---|---|
| 1 | 2.0000 | 0.0568 |
| 2 | 4.0000 | 0.1035 |
| 3 | 8.0000 | 0.2171 |



[ABS]=K1*[C]+K0

K0= 0.0000, K1= 0.0270

## Interference

# Beryllium (Be)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

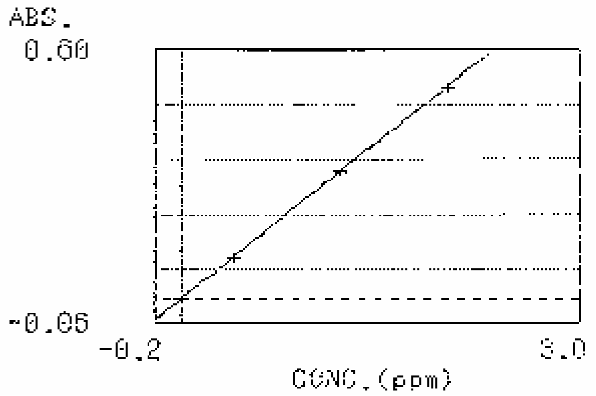
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 16 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 234.9 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 7.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 234.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0002 |
| 2 | 4.0000 | 0.1042 |
| 3 | 1.2000 | 0.3077 |
| 4 | 2.0000 | 0.5110 |



$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=1.0000$

K0= 0.0006, K1= 0.2582, K2= –0.0015

## Interference

Some ionization is made by the $N_2O$-$C_2H_2$ flame.

Interference by A*l* can be restrained by the addition of HF.

# Bismuth (Bi)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

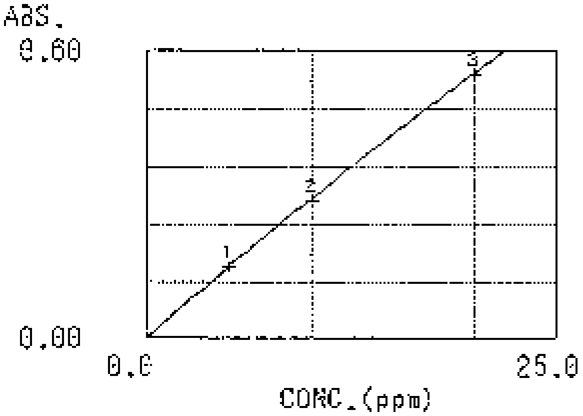
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/300 mA | Burner height | ; 7 mm |
| Wave length | ; 223.1 nm | ; 223.1 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.2 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGCD$_2$ mode

| STD. No. | CONC. (ppm) | ABS. 223.1nm |
|---|---|---|
| 1 | 5.0000 | 0.1526 |
| 2 | 10.0000 | 0.2901 |
| 3 | 20.0000 | 0.5527 |

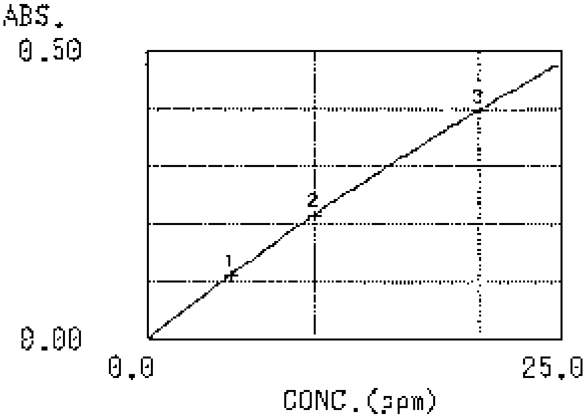


$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.0308, K2= –0.0002

- Calibration curve in BGC-SR mode

| STD. No. | CONC. (ppm) | ABS. 223.1nm |
|---|---|---|
| 1 | 5.0000 | 0.1088 |
| 2 | 10.0000 | 0.2113 |
| 3 | 20.0000 | 0.3955 |



$[ABS]=K2*[C]^2+K1*[C]+K$

K0= 0.0000, K1= 0.0225, K2= –0.0001

## Interference

Interference is small.

# Calcium (Ca) I

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

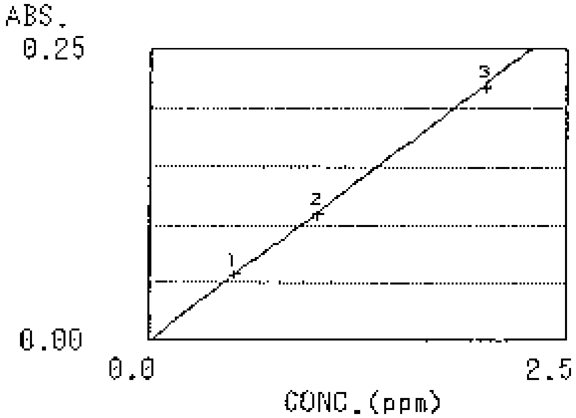
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 10 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 422.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 422.7nm |
|---|---|---|
| 1 | 0.5000 | 0.0565 |
| 2 | 1.0000 | 0.1096 |
| 3 | 2.0000 | 0.2179 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1093

## Interference

Negative interference is received if A*l*, Be, P, V, Si, Ti and Zr coexist. Therefore, 0.1 to 0.2% lanthanum chloride or strontium is added to the standard or unknown sample.

## Calcium (Ca) II

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

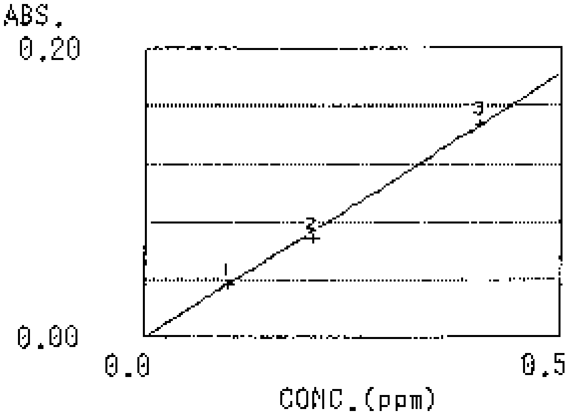
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 10 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 422.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 6.5 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>422.7nm |
|---|---|---|
| 1 | 0.1000 | 0.0368 |
| 2 | 0.2000 | 0.0696 |
| 3 | 0.4000 | 0.1479 |



[ABS]=K1*[C]+K0

K0= 0.0000, K1= 0.3655

### Interference

Negative interference, due to coexist substances in the Air-$C_2H_2$ flame, is removed by using the $N_2O$-$C_2H_2$ flame. However, it is ionized and 0.1 to 0.2% potassium chloride is added to the standard or unknown sample.

# Cadmium (Cd)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

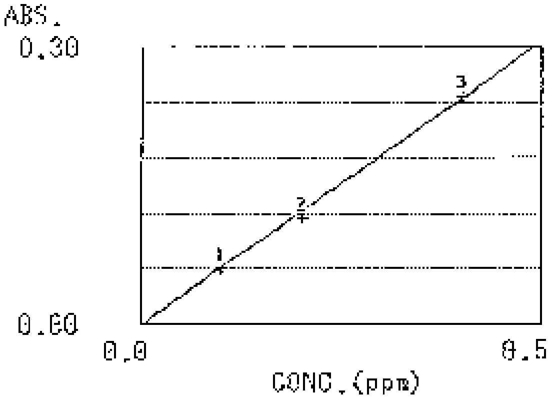
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 8 mA/0 mA | ; 8 mA/100 mA | Burner height | ; 7 mm |
| Wave length | ; 228.8 nm | ; 228.8 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

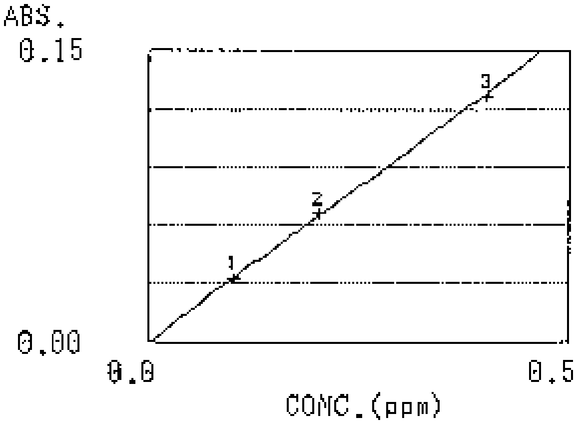
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>228.8nm |
|---|---|---|
| 1 | 0.1000 | 0.0605 |
| 2 | 0.2000 | 0.1153 |
| 3 | 0.4000 | 0.2478 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.6106

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>228.8nm |
|---|---|---|
| 1 | 0.1000 | 0.0329 |
| 2 | 0.2000 | 0.0659 |
| 3 | 0.4000 | 0.1272 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.3207

## Interference

Interference is small.

## Cobalt (Co)

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

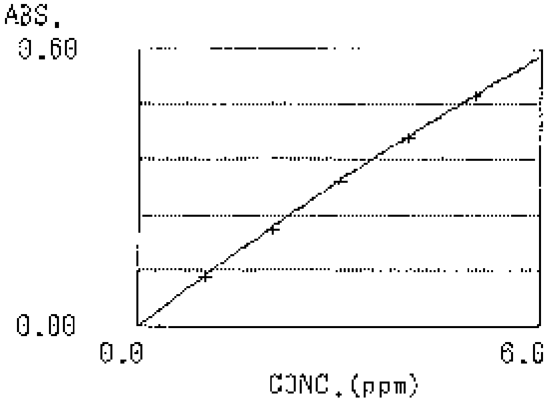
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 12 mA/400 mA | Burner height | ; 7 mm |
| Wave length | ; 240.7 nm | ; 240.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 2.2 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>240.7nm |
|---|---|---|
| 1 | 1.0000 | 0.1095 |
| 2 | 2.0000 | 0.2129 |
| 3 | 3.0000 | 0.3127 |
| 4 | 4.0000 | 0.4095 |
| 5 | 5.0000 | 0.4980 |

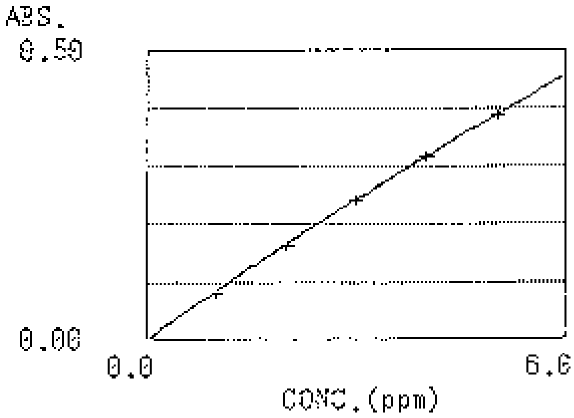


$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.1114, K2= –0.0023

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>240.7nm |
|---|---|---|
| 1 | 1.0000 | 0.0800 |
| 2 | 2.0000 | 0.1628 |
| 3 | 3.0000 | 0.2399 |
| 4 | 4.0000 | 0.3147 |
| 5 | 5.0000 | 0.3840 |



$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.0840, K2= 0.0014

### Interference

If excessive transition elements and heavy metals coexist, interference is given. For example, if nickel coexists (0.1% or so), 20 to 50% negative interference is obtained.

# Chromium (Cr)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

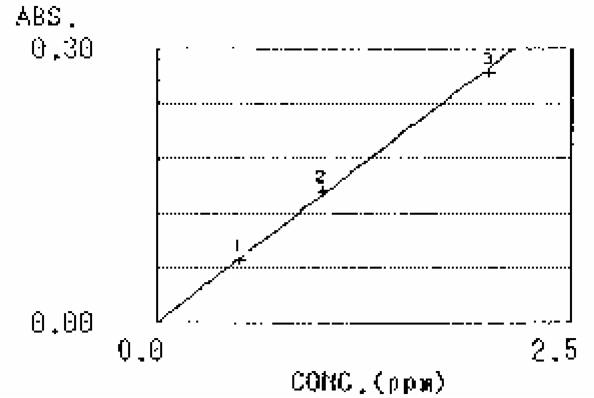
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/600 mA | Burner height | ; 9 mm |
| Wave length | ; 357.9 nm | ; 357.9 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

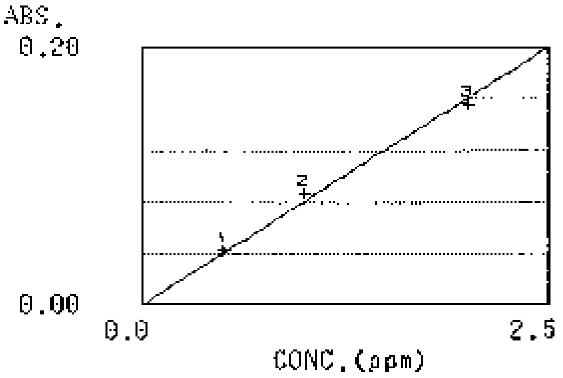
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>357.9nm |
|---|---|---|
| 1 | 0.5000 | 0.0692 |
| 2 | 1.0000 | 0.1463 |
| 3 | 2.0000 | 0.2742 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1389

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>357.9nm |
|---|---|---|
| 1 | 0.5000 | 0.0427 |
| 2 | 1.0000 | 0.0869 |
| 3 | 2.0000 | 0.1557 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0799

## Interference

Negative interference is given by Fe, which coexists in the Air-$C_2H_2$ flame. However, it can be removed by the addition of 0.1 to 0.2% ammonium chloride.

Interference from Cu, A*l*, Mg, Ba, etc. can be removed by the $N_2O$-$C_2H_2$ flame and can be restrained by changing the acetylene quantity.

# Copper (Cu)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

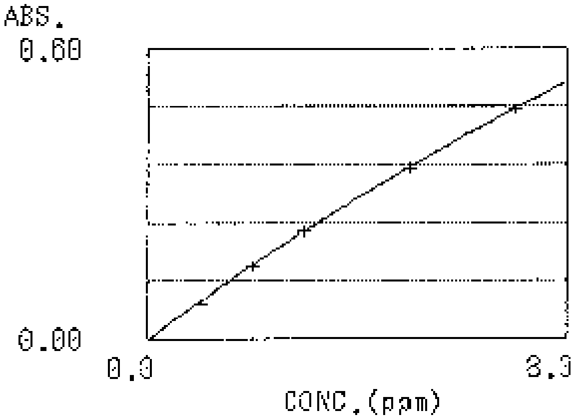
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 16 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 852.1 nm | Burner angle | ; 0 deg |
| Slit width | ; 1.0 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; HCL | Type of oxidant | ; air |

- Calibration curve in HCL mode (k500PPM addition)

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>852.1nm |
|---|---|---|
| 1 | 1.0000 | 0.0754 |
| 2 | 2.0000 | 0.1532 |
| 3 | 3.0000 | 0.2243 |
| 4 | 5.0000 | 0.3542 |
| 5 | 7.0000 | 0.4756 |



$[ABS]=K2*[C]^2+K1*[C]+K$

K0= 0.0000, K1= 0.0792, K2= –0.0016

## Interference

Ionization interference is great in the Air-$C_2H_2$ flame.

Therefore, 0.1% potassium (potassium chloride) is added to the standard or unknown sample as restrainer.

Thus, absorption sensitivity is almost doubled.

# Cesium (Cs)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

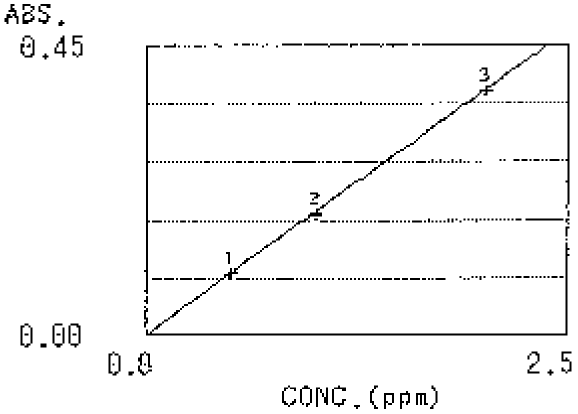
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 6 mA/0 mA | ; 6 mA/500 mA | Burner height | ; 7 mm |
| Wave length | ; 324.8 nm | ; 324.8 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

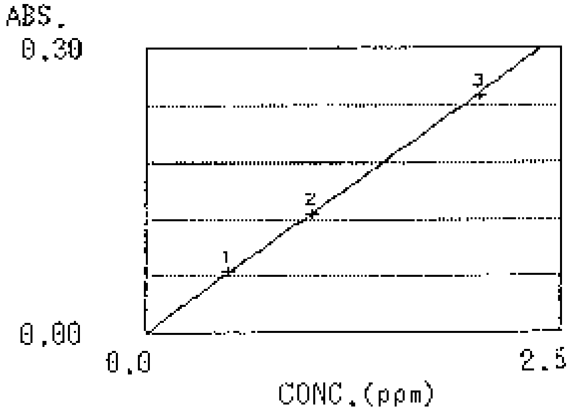
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>324.8nm |
|---|---|---|
| 1 | 0.5000 | 0.0968 |
| 2 | 1.0000 | 0.1898 |
| 3 | 2.0000 | 0.3800 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1901

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>324.8nm |
|---|---|---|
| 1 | 0.5000 | 0.0653 |
| 2 | 1.0000 | 0.1274 |
| 3 | 2.0000 | 0.2510 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1261

## Interference

Interference is small.

## Gallium (Ga)

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

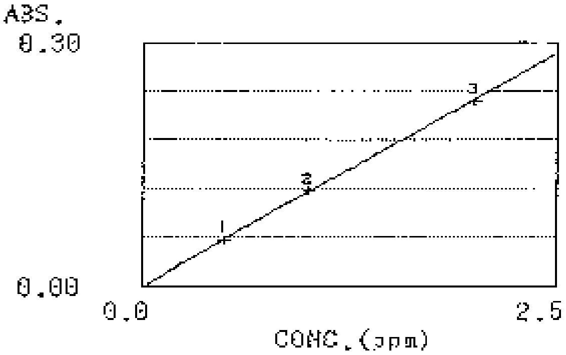
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 12 mA/400 mA | Burner height | ; 7 mm |
| Wave length | ; 248.3 nm | ; 248.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 2.2 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

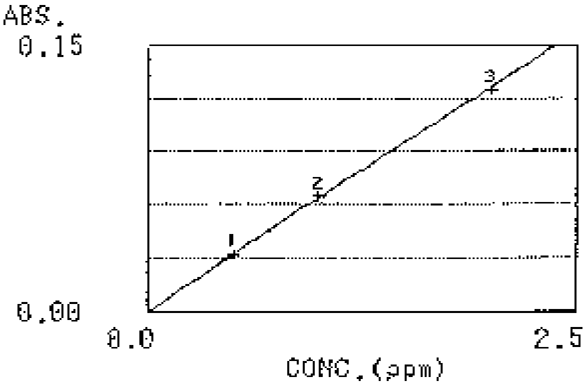
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>248.3nm |
|---|---|---|
| 1 | 0.5000 | 0.0569 |
| 2 | 1.0000 | 0.1167 |
| 3 | 2.0000 | 0.2285 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1147

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>248.3nm |
|---|---|---|
| 1 | 0.5000 | 0.0323 |
| 2 | 1.0000 | 0.0642 |
| 3 | 2.0000 | 0.1256 |



[ABS]=K1*[C]+K
K0= 0.0000, K1= 0.0632

### Interference

Slight interference is received if Ni, Co and mineral acid coexist.

Interference by Si can be removed by the addition of 0.1% calcium chloride. Interference by citric acid can be restrained by the addition of 0.1 to 0.2% phosphoric acid.

# Iron (Fe)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

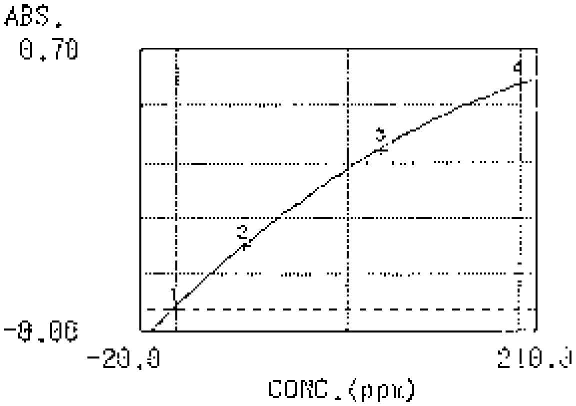
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 4 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 294.4 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>294.4nm |
|---|---|---|
| 1 | 0.0000 | 0.0020 |
| 2 | 40.0000 | 0.1704 |
| 3 | 120.0000 | 0.4333 |
| 4 | 200.0000 | 0.6074 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=1.0000
K0= 0.0025, K1= 0.0045, K2= –0.0000

## Interference

# Germanium (Ge)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

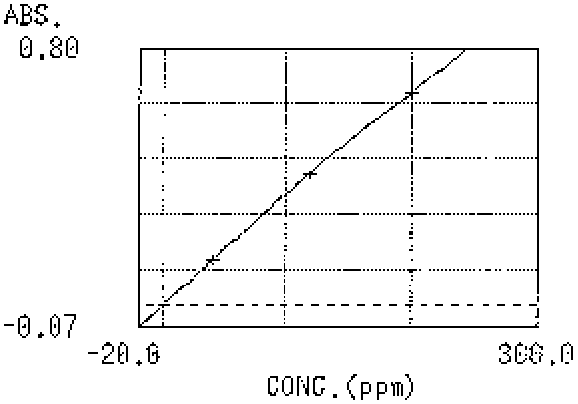
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 18 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 265.2 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 7.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 265.2nm |
|---|---|---|
| 1 | 0.0000 | –0.0016 |
| 2 | 40.0000 | 0.1383 |
| 3 | 120.0000 | 0.4034 |
| 4 | 200.0000 | 0.6627 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=1.0000
K0= 0.0008, K1= 0.0035, K2= –0.0000

## Interference

Interference is small.

## Potassium (K)

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

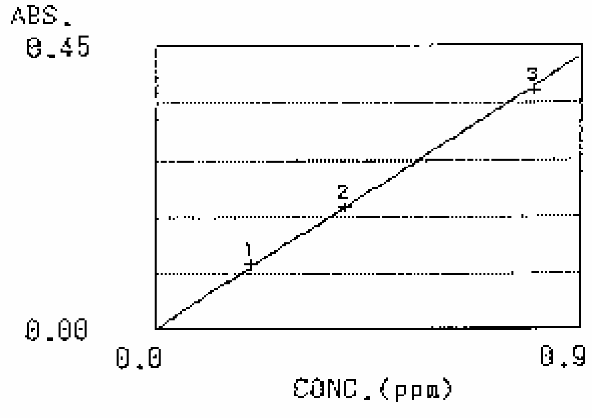
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 8 mA/600 mA | Burner height | ; 7 mm |
| Wave length | ; 766.5 nm | ; 766.5 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; HCL | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in HCL mode

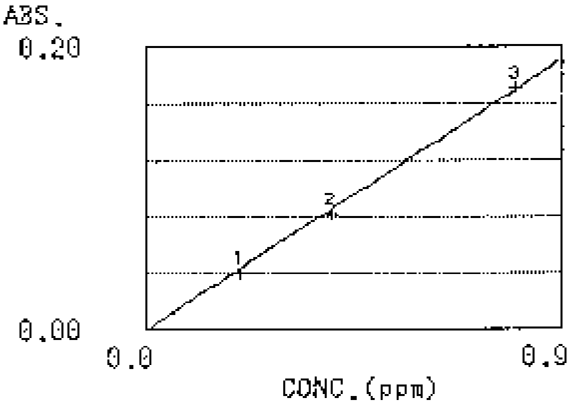
| STD. No. | CONC. (ppm) | ABS. 766.5nm |
|---|---|---|
| 1 | 0.2000 | 0.1049 |
| 2 | 0.4000 | 0.1962 |
| 3 | 0.8000 | 0.3820 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.4822

- Calibration curve in BGC-SR mode

| STD. No. | CONC. (ppm) | ABS. 766.5nm |
|---|---|---|
| 1 | 0.2000 | 0.0405 |
| 2 | 0.4000 | 0.0827 |
| 3 | 0.8000 | 0.1718 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.2126

### Interference

Because it is ionized to some degree, 0.1 to 0.2% cesium chloride or rubidium chloride is added to the standard or unknown sample.

# Lithium (Li)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

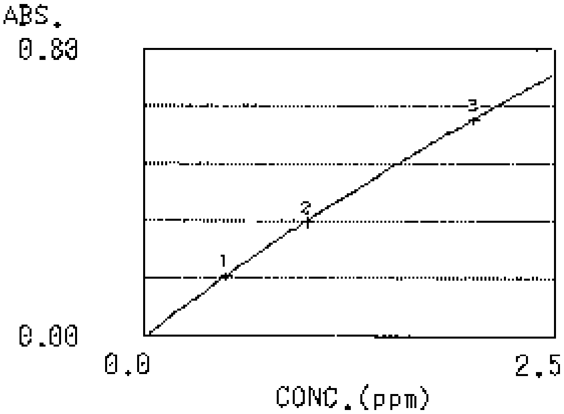
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 8 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 670.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; HCL | Type of oxidant | ; air |

- Calibration curve in HCL mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>670.7nm |
|---|---|---|
| 1 | 0.5000 | 0.1681 |
| 2 | 1.0000 | 0.3171 |
| 3 | 2.0000 | 0.6025 |



$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.3385, K2= –0.0187

## Interference

Because it is ionized by the Air-$C_2H_2$ flame, 0.1% potassium chloride is added to the standard or unknown sample as a restrainer.

# Magnesium (Mg)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

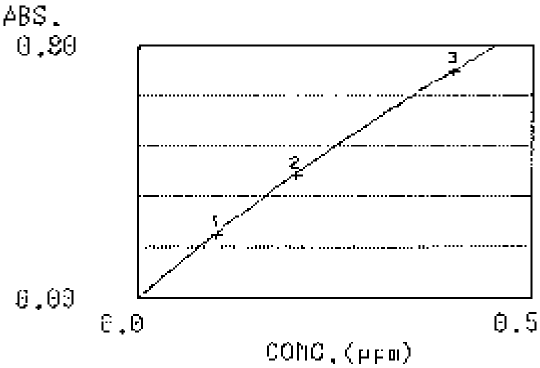
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 8 mA/0 mA | ; 8 mA/500 mA | Burner height | ; 7 mm |
| Wave length | ; 285.2 nm | ; 285.2 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>285.2nm |
|---|---|---|
| 1 | 0.1000 | 0.2028 |
| 2 | 0.2000 | 0.3898 |
| 3 | 0.4000 | 0.7201 |

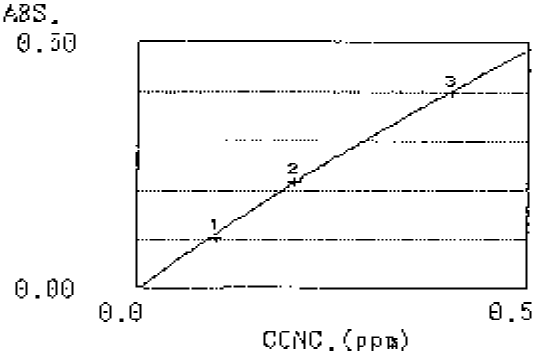


[ABS]=K2*[C]$^2$+K1*[C]+K0

K0= 0.0000, K1= 2.1000, K2= –0.7497

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>285.2nm |
|---|---|---|
| 1 | 0.1000 | 0.1016 |
| 2 | 0.2000 | 0.2151 |
| 3 | 0.4000 | 0.3971 |



[ABS]=K2*[C]$^2$+K1*[C]+K0

K0= 0.0000, K1= 1.1083, K2= –0.2839

## Interference

A negative interference is given if P, A*l*, Ti and Si are put in the form of an oxyacid, and coexist in the same or more quantity than Mg. This interference is retrained by the addition of 0.1% strontium chloride to the standard or unknown sample.

There is no interference of the above elements in the $N_2O$-$C_2H_2$ flame. However, it is ionized and 0.1% potassium chloride or strontium chloride is added to the standard or unknown sample.

# Manganese (Mn)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

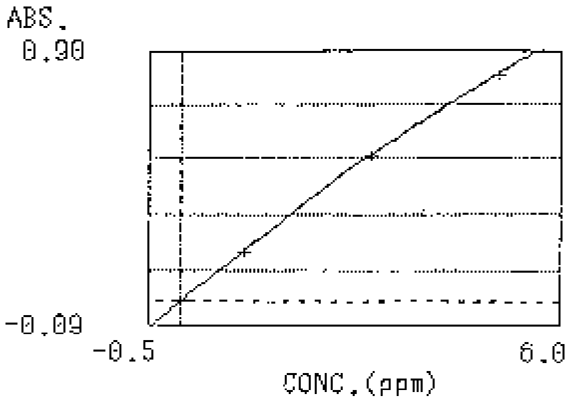
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/600 mA | Burner height | ; 7 mm |
| Wave length | ; 279.5 nm | ; 279.5 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

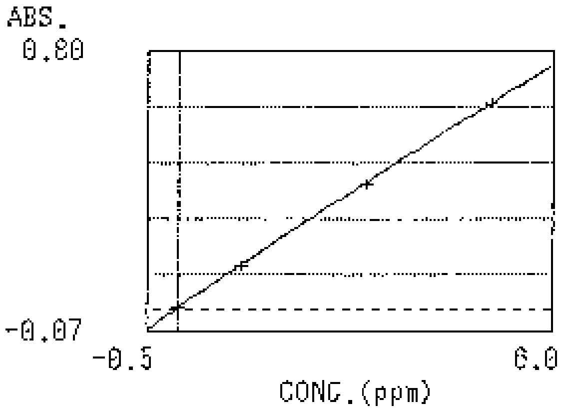
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | –0.0010 |
| 2 | 1.0000 | 0.1795 |
| 3 | 3.0000 | 0.5201 |
| 4 | 5.0000 | 0.8169 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=1.0000$
K0= 0.0020, K1= 0.1883, K2= –0.0049

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0031 |
| 2 | 1.0000 | 0.1359 |
| 3 | 3.0000 | 0.3935 |
| 4 | 5.0000 | 0.6378 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=1.0000$
K0= 0.0029, K1= 0.1348, K2= –0.0016

## Interference

Small interference.

Because Si gives a negative interference, 0.1% calcium chloride is added.

# Molybdenum (Mo)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

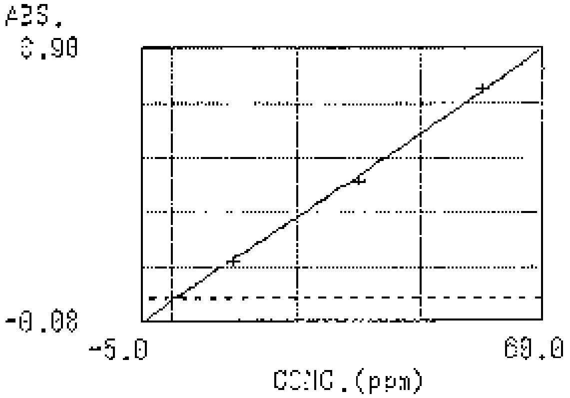
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 10 mA/500 mA | Burner height | ; 17 mm |
| Wave length | ; 313.3 nm | ; 313.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 7.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

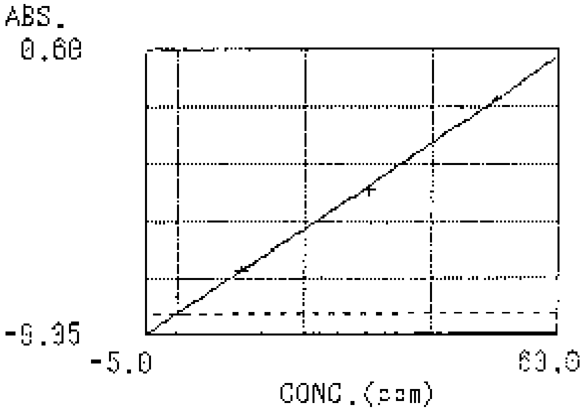
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>313.3nm |
|---|---|---|
| 1 | 0.0000 | –0.0003 |
| 2 | 10.0000 | 0.1368 |
| 3 | 30.0000 | 0.4219 |
| 4 | 50.0000 | 0.7551 |



[ABS]=K1*[C]+K0 $r^2$=0.9981
K0= –0.0107, K1= 0.0151

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>313.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0003 |
| 2 | 10.0000 | 0.0998 |
| 3 | 30.0000 | 0.2827 |
| 4 | 50.0000 | 0.4908 |



[ABS]=K1*[C]+K0 $r^2$=0.9992
K0= –0.0007, K1= 0.0097

## Interference

The interference is not clear but 0.5% aluminum chloride or 2% ammonium chloride is added to remove sensitivity differences due to the burner height.

# Sodium (Na)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

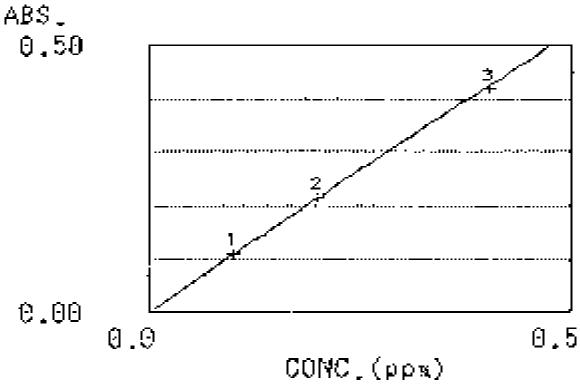
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 8 mA/600 mA | Burner height | ; 7 mm |
| Wave length | ; 589.0 nm | ; 589.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; HCL | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in HCL mode

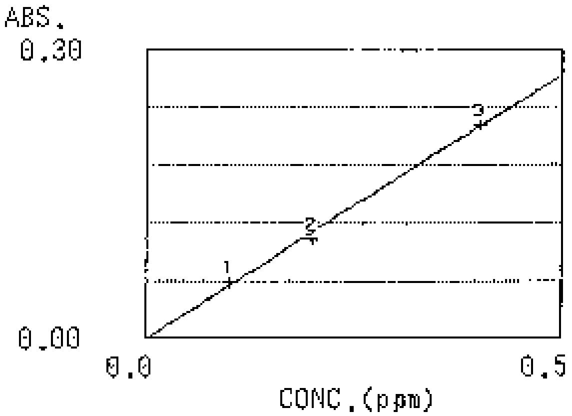
| STD. No. | CONC. (ppm) | ABS. 589.0nm |
|---|---|---|
| 1 | 0.1000 | 0.1098 |
| 2 | 0.2000 | 0.2119 |
| 3 | 0.4000 | 0.4190 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 1.0522

- Calibration curve in BGC-SR mode

| STD. No. | CONC. (ppm) | ABS. 589.0nm |
|---|---|---|
| 1 | 0.1000 | 0.0585 |
| 2 | 0.2000 | 0.1035 |
| 3 | 0.4000 | 0.2204 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.5462

## Interference

Ionization by the Air-$C_2H_2$ flame can be decreased by adding 0.1% potassium chloride or cesium chloride to the standard or unknown sample.

# Nickel (Ni)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

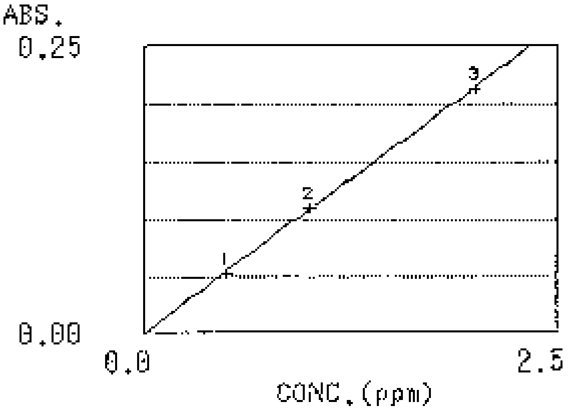
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 12 mA/400 mA | Burner height | ; 7 mm |
| Wave length | ; 232.0 nm | ; 232.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | ; 0.2 nm | Fuel gas flow | ; 2.2 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

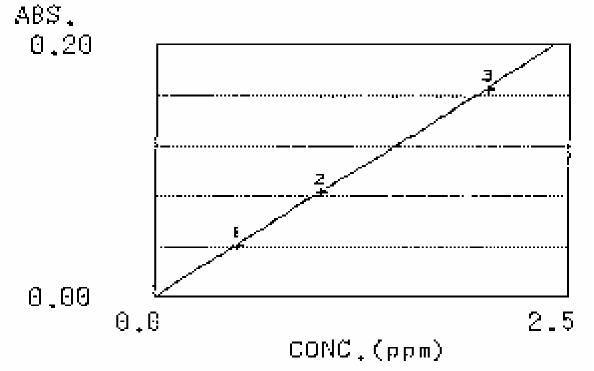
| STD. No. | CONC. (ppm) | ABS. 232.0nm |
|---|---|---|
| 1 | 0.5000 | 0.0523 |
| 2 | 1.0000 | 0.1086 |
| 3 | 2.0000 | 0.2126 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.1067

- Calibration curve in BGC-SR mode

| STD. No. | CONC. (ppm) | ABS. 232.0nm |
|---|---|---|
| 1 | 0.5000 | 0.0418 |
| 2 | 1.0000 | 0.0834 |
| 3 | 2.0000 | 0.1661 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0831

## Interference

A negative interference is received if high concentrations of Fe and Cr coexist.

The 232.0 nm calibration curve bends at high concentrations owing to Ni232.14 nm. The 341.5 and 352.4 nm wavelengths are suitable for the high concentration calibration curve. (Refer to Section 1 - 2 - 2.1.a.)

# Lead (Pb) I

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

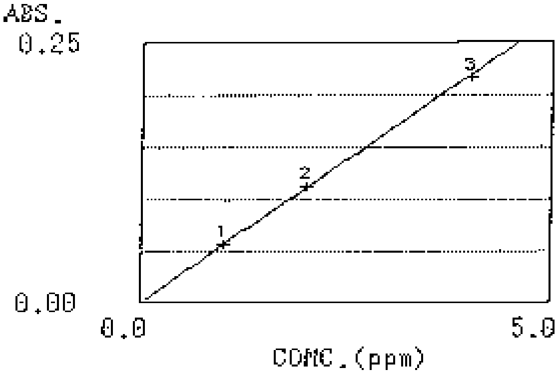
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 8 mA/300 mA | Burner height | ; 7 mm |
| Wave length | ; 217.0 nm | ; 217.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

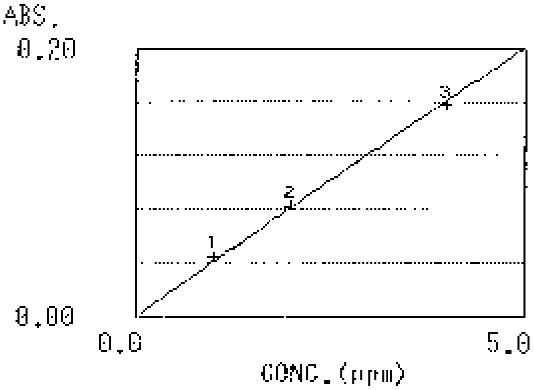
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>217.0nm |
|---|---|---|
| 1 | 1.0000 | 0.0567 |
| 2 | 2.0000 | 0.1119 |
| 3 | 4.0000 | 0.2160 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0545

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>217.0nm |
|---|---|---|
| 1 | 1.0000 | 0.0452 |
| 2 | 2.0000 | 0.0827 |
| 3 | 4.0000 | 0.1581 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0401

## Interference

A higher interference is given if 1% or more of the ion element coexists in a 5 ppm of Pb.

Because a negative interference is given if a 10-fold carbonate, phosphate, iodine compound, or fluorine compound coexist, 0.1M EDTA is added.

## Lead (Pb) II

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

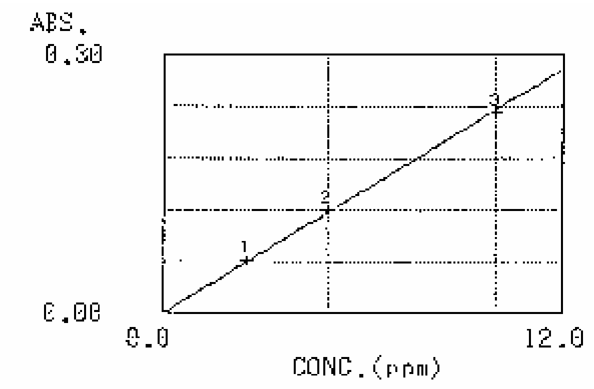
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 10 mA/0 mA | ; 8 mA/300 mA | Burner height | ; 7 mm |
| Wave length | ; 283.3 nm | ; 283.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

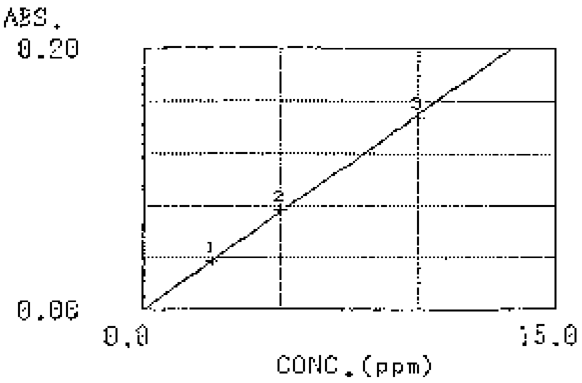
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>283.3nm |
|---|---|---|
| 1 | 2.5000 | 0.0622 |
| 2 | 5.0000 | 0.1207 |
| 3 | 10.0000 | 0.2327 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0235

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>283.3nm |
|---|---|---|
| 1 | 2.5000 | 0.0382 |
| 2 | 5.0000 | 0.0770 |
| 3 | 10.0000 | 0.1479 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.0149

### Interference

A higher interference is given if 1% or more of the ion element coexists in a 5 ppm of Pb.

Because a negative interference is given if a 10-fold carbonate, phosphate, iodine compound, or fluorine compound coexist, 0.1M EDTA is added.

# Palladium (Pd)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

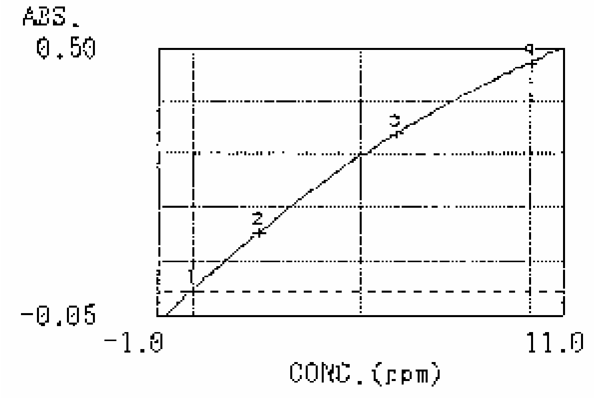
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 10 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 244.8 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>244.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0005 |
| 2 | 2.0000 | 0.1183 |
| 3 | 6.0000 | 0.3205 |
| 4 | 10.0000 | 0.4720 |



[ABS]=K2*$[C]^2$+K1*[C]+K0  $r^2$=1.0000

K0= 0.0001, K1= 0.0625, K2= –0.0015

## Interference

If A*l*, Co or Ni coexists, 0.1 to 0.5% EDTA is added.

# Platinum (Pt)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

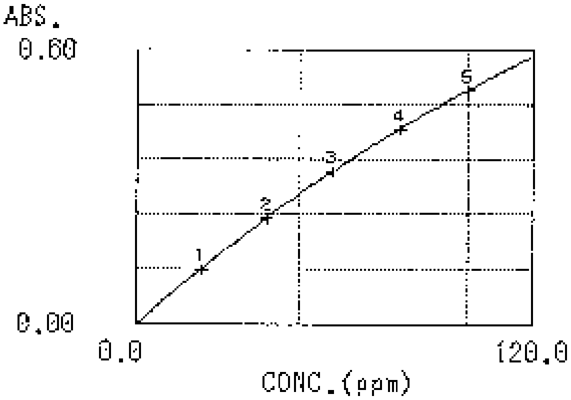
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 14 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 266.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 266.0nm |
|---|---|---|
| 1 | 20.0000 | 0.1194 |
| 2 | 40.0000 | 0.2319 |
| 3 | 60.0000 | 0.3346 |
| 4 | 80.0000 | 0.4239 |
| 5 | 100.0000 | 0.5127 |



$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.0062, K2= –0.0000

## Interference

Sensitivity is affected if other precious metals coexist, and the effect can be reduced by the addition of 0.1 to 0.2% lanthanum chloride.

# Rubidium (Rb)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

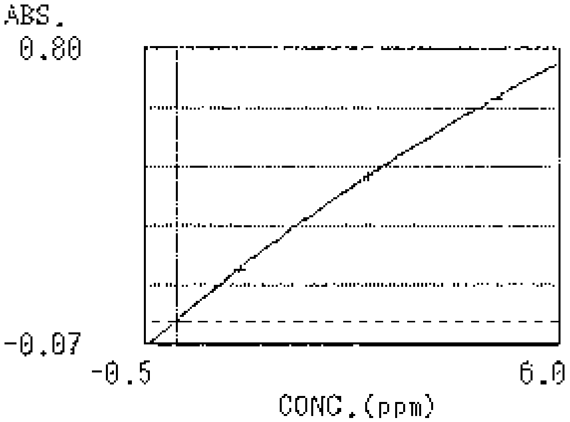
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 14 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 780.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; HCL | Type of oxidant | ; air |

- Calibration curve in HCL mode

| STD. No. | CONC. (ppm) | ABS. 780.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0002 |
| 2 | 1.0000 | 0.1500 |
| 3 | 3.0000 | 0.4255 |
| 4 | 5.0000 | 0.6563 |



$[ABS]=K2*[C]^2+K1*[C]+K0$ $r^2=1.0000$

K0= 0.0005, K1= 0.1571, K2= –0.0051

## Interference

## Rhodium (Rh)

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

### Measuring conditions and Calibration curve

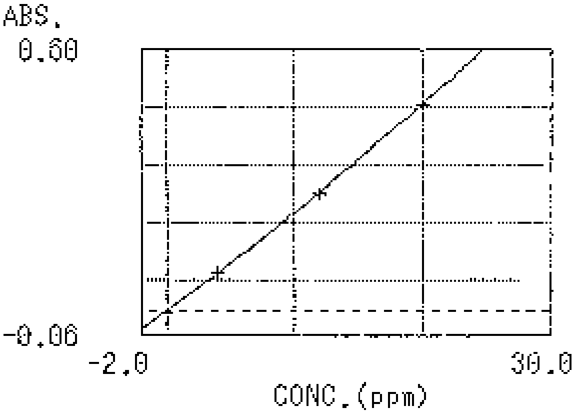
- Measuring conditions

Current ; 12 mA/0 mA
Wave length ; 343.5 nm
Slit width ; 0.5 nm
Lighting mode ; BGC-$D_2$

Burner height ; 7 mm
Burner angle ; 0 deg
Fuel gas flow ; 2.1 *l*/min
Type of oxidant ; air

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>343.5nm |
|---|---|---|
| 1 | 0.0000 | –0.0021 |
| 2 | 4.0000 | 0.0935 |
| 3 | 12.0000 | 0.2708 |
| 4 | 20.0000 | 0.4774 |



$[ABS]=K2*[C]^2+K1*[C]+K0$ $r^2=0.9996$
K0= 0.0008, K1= 0.0213, K2= 0.0001

### Interference

# Antimony (Sb)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

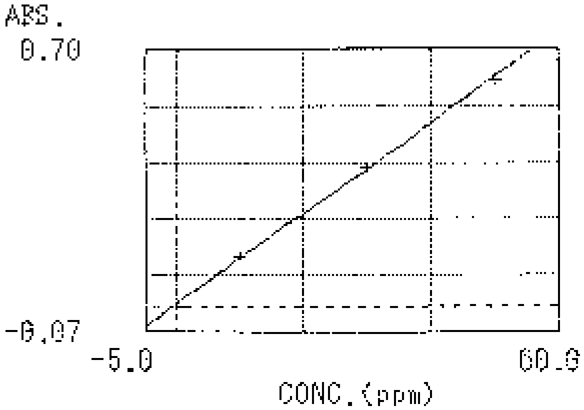
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 13 mA/0 mA | ; 15 mA/500 mA | Burner height | ; 7 mm |
| Wave length | ; 217.6 nm | ; 217.6 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-D$_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGCD$_2$ mode

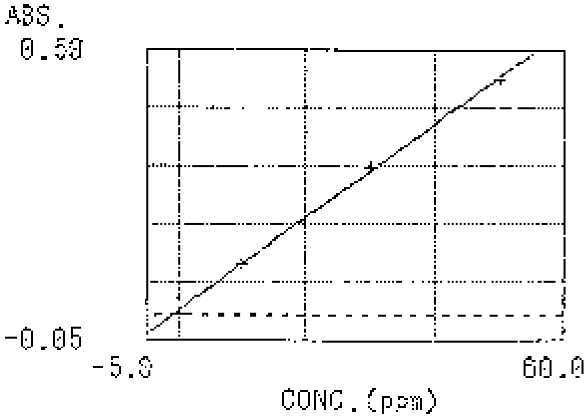
| STD. No. | CONC. (ppm) | ABS. 217.6nm |
|---|---|---|
| 1 | 0.0000 | –0.0011 |
| 2 | 10.0000 | 0.1332 |
| 3 | 30.0000 | 0.3866 |
| 4 | 50.0000 | 0.6175 |



[ABS]=K1*[C]+K0 $r^2$=0.9991
K0=-0.0058, K1= 0.0124

- Calibration curve in BGC-SR mode

| STD. No. | CONC. (ppm) | ABS. 217.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0020 |
| 2 | 10.0000 | 0.0965 |
| 3 | 30.0000 | 0.2773 |
| 4 | 50.0000 | 0.4435 |



[ABS]=K1*[C]+K0 $r^2$=0.9993
K0=-0.0061, K1= 0.0088

## Interference

Spectroscopic interference is received if Cd or Cu coexists in high concentrations.

# Selenium (Se)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

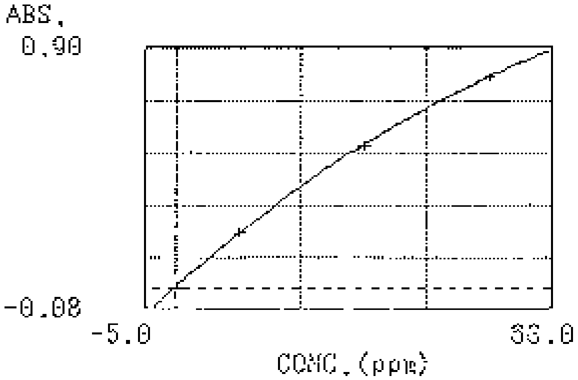
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 23 mA/0 mA | Burner height | ; 15 mm |
| Wave length | ; 196.0 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 3.7 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC-$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 196.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0007 |
| 2 | 10.0000 | 0.2045 |
| 3 | 30.0000 | 0.5343 |
| 4 | 50.0000 | 0.7898 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999
K0= 0.0024, K1= 0.0209, K2= –0.0001

## Interference

# Silicon (Si)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

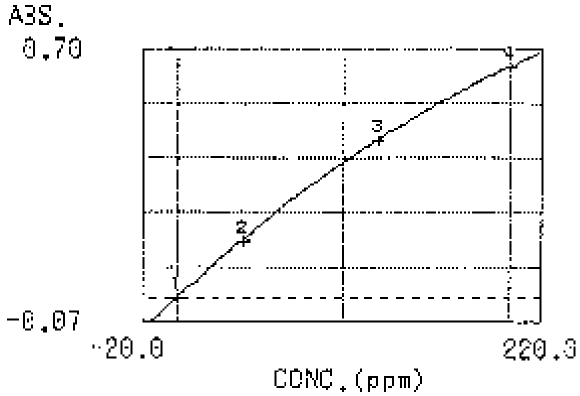
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 15 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 251.6 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 7.7 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC-$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 251.6nm |
|---|---|---|
| 1 | 0.0000 | –0.0009 |
| 2 | 40.0000 | 0.1592 |
| 3 | 120.0000 | 0.4460 |
| 4 | 200.0000 | 0.6495 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999
K0= 0.0033, K1= 0.0044, K2= –0.0000

## Interference

Ionization can be removed by the addition of 0.1% potassium chloride or sodium chloride. Silicon absorption can be restrained under 1% coexistence of HF, boric acid and potassium.

# Tin (Sn) I

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

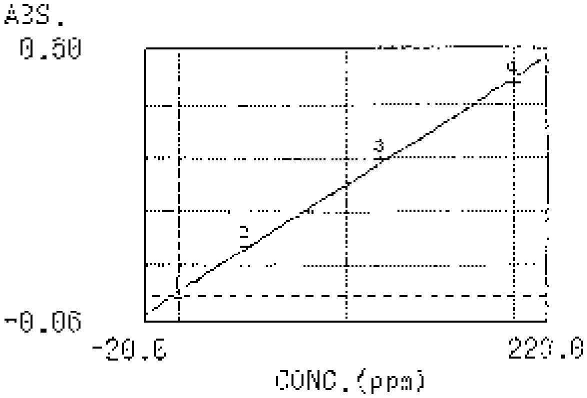
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 14 mA/0 mA | ; 20 mA/500 mA | Burner height | ; 9 mm |
| Wave length | ; 224.6 nm | ; 224.6 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 3.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

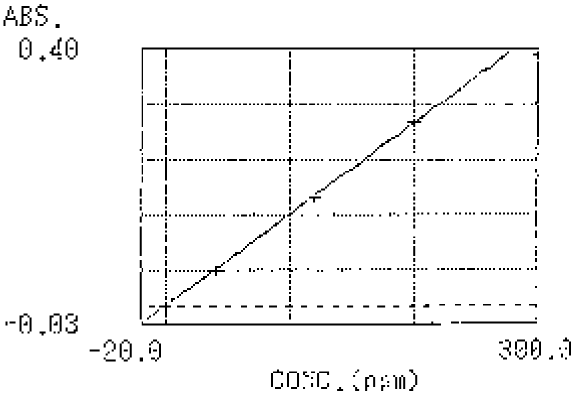
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>224.6nm |
|---|---|---|
| 1 | 0.0000 | –0.0031 |
| 2 | 40.0000 | 0.1219 |
| 3 | 120.0000 | 0.3357 |
| 4 | 200.0000 | 0.5204 |



[ABS]=K1*[C]+K0 $r^2$=0.9968
K0= –0.0092, K1= 0.0026

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>224.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0002 |
| 2 | 40.0000 | 0.0578 |
| 3 | 120.0000 | 0.1704 |
| 4 | 200.0000 | 0.2860 |



[ABS]=K1*[C]+K0 $r^2$=1.0000
K0=-0.0002, K1= 0.0014

## Interference

# Tin (Sn) II

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

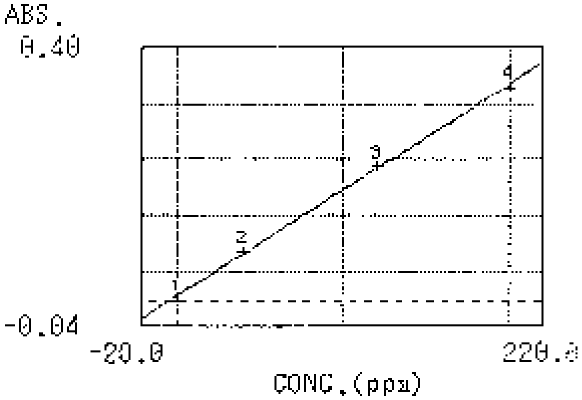
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | | |
|---|---|---|---|---|---|
| Current | ; | 10 mA/0 mA | Burner height | ; | 9 mm |
| Wave length | ; | 286.3 nm | Burner angle | ; | 0 deg |
| Slit width | ; | 0.5 nm | Fuel gas flow | ; | 3.0 *l*/min |
| Lighting mode | ; | BGC-$D_2$ | Type of oxidant | ; | air |

- Calibration curve in BGC-$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 286.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0003 |
| 2 | 40.0000 | 0.0785 |
| 3 | 120.0000 | 0.2118 |
| 4 | 200.0000 | 0.3378 |



[ABS]=K1*[C]+K0 $r^2$=0.9986
K0= 0.0063, K1= 0.0017

## Interference

# Tin (Sn) III

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

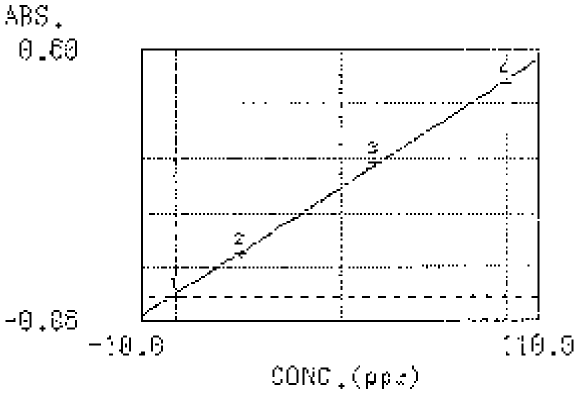
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 14 mA/0 mA | ; 20 mA/500 mA | Burner height | ; 17 mm |
| Wave length | ; 224.6 nm | ; 224.6 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 6.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC-$D_2$ mode

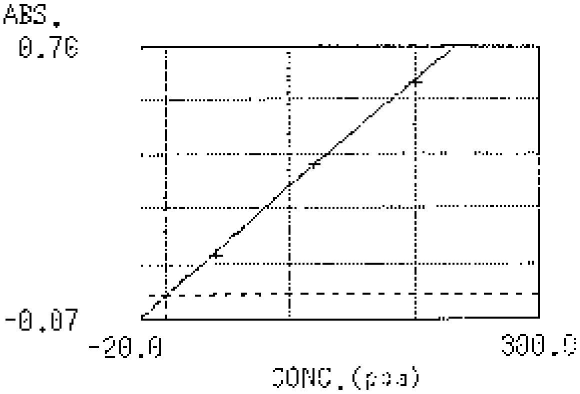
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>224.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0000 |
| 2 | 20.0000 | 0.1113 |
| 3 | 60.0000 | 0.3253 |
| 4 | 100.0000 | 0.5162 |



[ABS]=K1*[C]+K0 $r^2$=0.9989
K0= –0.0057, K1= 0.0052

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>224.6nm |
|---|---|---|
| 1 | 0.0000 | –0.0025 |
| 2 | 40.0000 | 0.1115 |
| 3 | 120.0000 | 0.3639 |
| 4 | 200.0000 | 0.5996 |



[ABS]=K1*[C]+K0 $r^2$=0.9997
K0= –0.0046, K1= 0.0030

## Interference

Interference from other elements is hardly received.

# Tin (Sn) IV

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

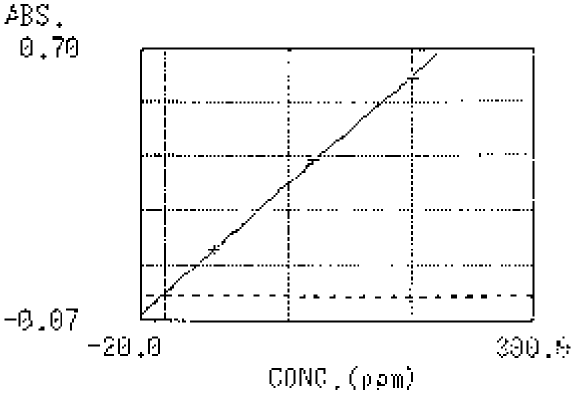
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 14 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 286.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 6.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve by BGC-$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>286.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0009 |
| 2 | 40.0000 | 0.1335 |
| 3 | 120.0000 | 0.3817 |
| 4 | 200.0000 | 0.6154 |



[ABS]=K1*[C]+K0  $r^2$=0.9995
K0= 0.0068, K1= 0.0031

## Interference

Interference from other elements is hardly received.

# Strontium (Sr)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

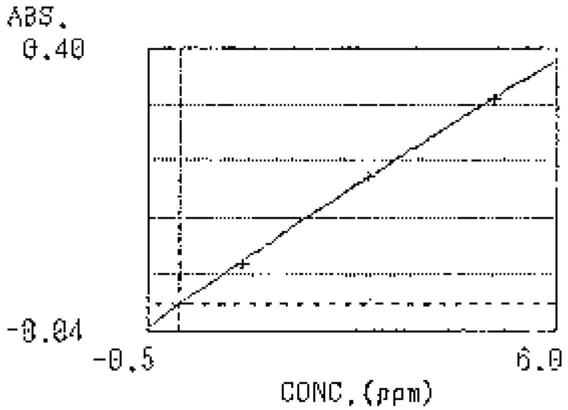
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 8 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 460.7 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; HCL | Type of oxidant | ; air |

- Calibration curve in HCL mode

| STD. No. | CONC. (ppm) | ABS. 460.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0011 |
| 2 | 1.0000 | 0.0645 |
| 3 | 3.0000 | 0.1993 |
| 4 | 5.0000 | 0.3208 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9998$

K0= 0.0004, K1= 0.0684, K2= –0.0008

## Interference

If Si, A*l*, Ti, Zr, P, etc. coexist in the Air-$C_2H_2$ flame, a negative interference is received. 0.5% lanthanum chloride or calcium chloride is added to the standard or unknown sample.

No interference is received by the $N_2O$-$C_2H_2$ flame, but ionization occurs. Therefore, 0.5% potassium chloride is added to the standard or unknown sample.

# Tellurium (Te)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

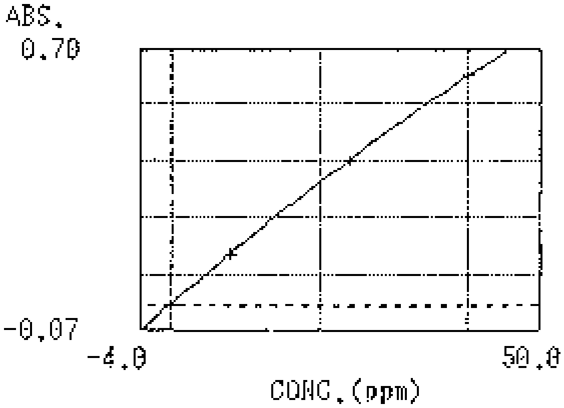
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 14 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 214.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.2 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC-$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>286.3nm |
|---|---|---|
| 1 | 0.0000 | –0.0015 |
| 2 | 8.0000 | 0.1400 |
| 3 | 24.0000 | 0.3925 |
| 4 | 40.0000 | 0.6233 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=1.0000

K0= –0.0004, K1= 0.0177, K2= –0.0000

## Interference

## Titanium (Ti)

### Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

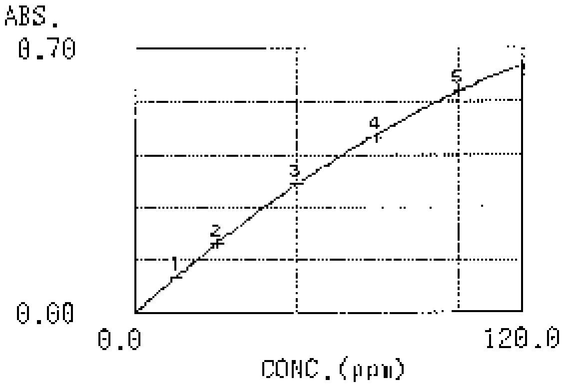
### Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 12 mA/0 mA | ; 10 mA/600 mA | Burner height | ; 17 mm |
| Wave length | ; 364.3 nm | ; 364.3 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 7.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>364.3nm |
|---|---|---|
| 1 | 12.0000 | 0.0951 |
| 2 | 25.0000 | 0.1838 |
| 3 | 50.0000 | 0.3425 |
| 4 | 75.0000 | 0.4667 |
| 5 | 100.0000 | 0.5879 |

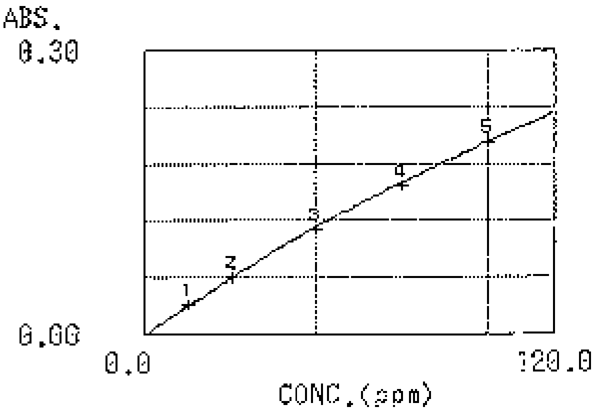


$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= 0.0000, K1= 0.0077, K2= –0.0000

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>364.3nm |
|---|---|---|
| 1 | 12.5000 | 0.0325 |
| 2 | 25.0000 | 0.0611 |
| 3 | 50.0000 | 0.1106 |
| 4 | 75.0000 | 0.1573 |
| 5 | 100.0000 | 0.2044 |



$[ABS]=K2*[C]^2+K1*[C]+K0$

K0= –0.0000, K1= 0.0024, K2= –0.0000

### Interference

If excessive hydrofluoric acid, $F_2$ or A*l* coexists, sensitivity rises. Therefore, 0.1M ammonium fluoride is added to the standard or unknown sample.

0.1% potassium chloride is added to restrain ionization.

# Thallium (T*l*)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

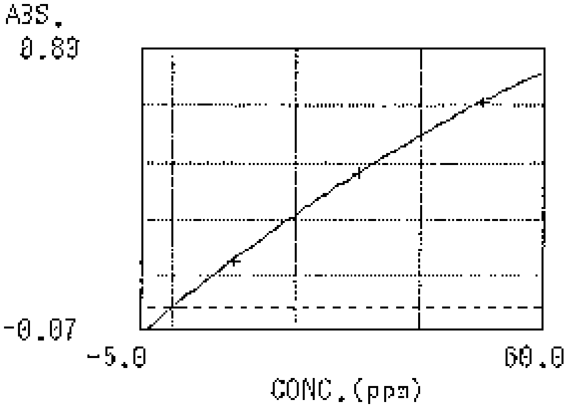
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 6 mA/0 mA | Burner height | ; 7 mm |
| Wave length | ; 276.8 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 1.8 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; air |

- Calibration curve in BGC-$D_2$ mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>276.8nm |
|---|---|---|
| 1 | 0.0000 | –0.0019 |
| 2 | 10.0000 | 0.1522 |
| 3 | 30.0000 | 0.4248 |
| 4 | 50.0000 | 0.6394 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=1.0000$
K0= –0.0026, K1= 0.0163, K2= –0.0000

## Interference

Interference hardly exists.

# Vanadium (V)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

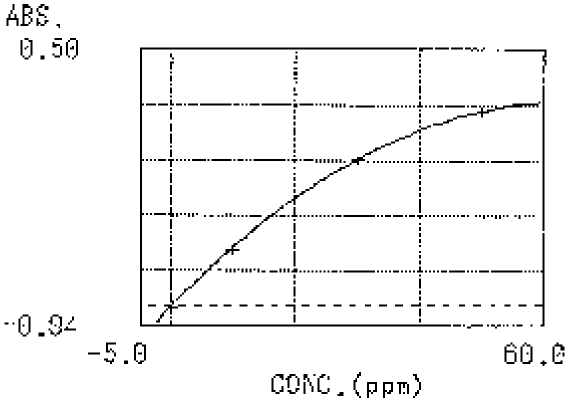
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | |
|---|---|---|---|
| Current | ; 10 mA/0 mA | Burner height | ; 17 mm |
| Wave length | ; 318.4 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | Fuel gas flow | ; 7.5 *l*/min |
| Lighting mode | ; BGC-$D_2$ | Type of oxidant | ; $N_2O$ |

- Calibration curve in BGC-$D_2$ mode

| STD. No. | CONC. (ppm) | ABS. 318.4nm |
|---|---|---|
| 1 | 0.0000 | –0.0010 |
| 2 | 10.0000 | 0.1122 |
| 3 | 30.0000 | 0.2886 |
| 4 | 50.0000 | 0.3826 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=0.9999

K0= –0.0020, K1= 0.0126, K2= –0.0000

## Interference

Sensitivity rises if a lot of A*l*, Ti, excessive Fe, or phosphoric acid coexists. If these elements are the main components, the matrix of the standard and unknown samples is matched.

0.1% potassium chloride is added to restrain ionization.

# Zinc (Zn)

## Standard substance and standard solution preparation method

Refer to Section 2 - 3 for the Standard solution preparation method

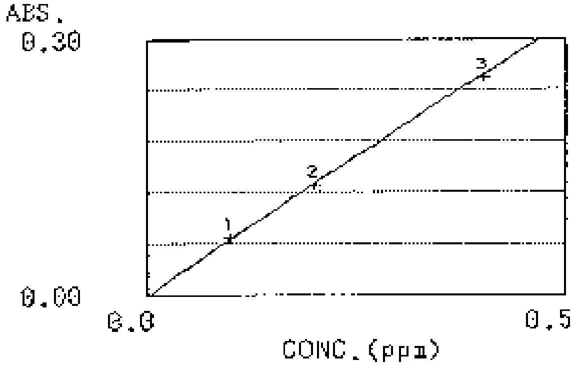
## Measuring conditions and Calibration curve

- Measuring conditions

| | | | | |
|---|---|---|---|---|
| Current | ; 8 mA/0 mA | ; 10 mA/300 mA | Burner height | ; 7 mm |
| Wave length | ; 213.9 nm | ; 213.9 nm | Burner angle | ; 0 deg |
| Slit width | ; 0.5 nm | ; 0.5 nm | Fuel gas flow | ; 2.0 *l*/min |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR | Type of oxidant | ; air |

- Calibration curve in BGC$D_2$ mode

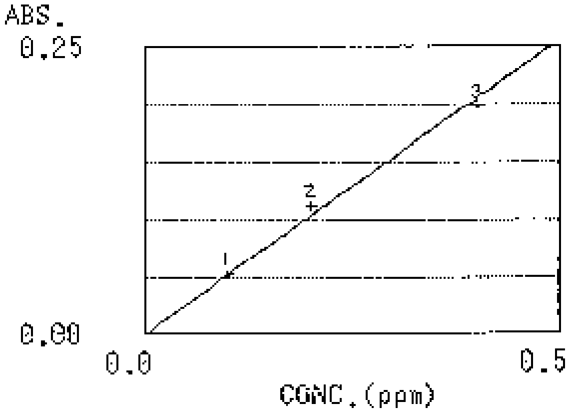
| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>213.9nm |
|---|---|---|
| 1 | 0.1000 | 0.0678 |
| 2 | 0.2000 | 0.1297 |
| 3 | 0.4000 | 0.2558 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.6430

- Calibration curve in BGC-SR mode

| STD.<br>No. | CONC.<br>(ppm) | ABS.<br>213.9nm |
|---|---|---|
| 1 | 0.1000 | 0.0526 |
| 2 | 0.2000 | 0.1118 |
| 3 | 0.4000 | 0.1986 |



[ABS]=K1*[C]+K0
K0= 0.0000, K1= 0.5098

## Interference

Interference hardly exists.

# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 4

## Measuring Conditions by Element of Furnace Analysis Method

SHIMADZU CORPORATION

## Atomic Absorption Spectrophotometer Cookbook

## Section 4

# CONTENTS

# 7. Measuring conditions by element of furnace analysis method

## 7.1 Measuring conditions

The solution prepared based on the standard sample preparation method (cookbook section 2 - 3) was used to make the calibration curve in the standard concentration range. Analysis conditions stored in AA-6401 or 6501 were mainly used. HCL, BGC-$D_2$, and BGC-SR methods were used according to the respective element. The relationship between the ashing temperature, the atomization temperature, and sensitivity is also shown. However, they are omitted for some elements.

According to the data, a Step heating stage comes after the Ramp heating stage. Better repeatability can be expected by inserting another Ramp heating stage up to the Ashing temperature between the two. A cleaning stage is set after the Atomization stage it necessary.

The high-density graphite tube or the pyrolytic graphite tube was used depending on the characteristic of each element and its selection is written in each data.

As the atomization condition, there are two modes: the standard mode (0. 0) and the high sensitivity mode (0. 0H) are available and two types of data are shown.

The standard mode and high sensitivity mode are used as shown below.

- Standard mode (0. 0)

  The absorbance sensitivity is 1/3 to 1/2 of that obtained in the high sensitivity mode, depending on the element.

  However, this mode is effective for the measurement of the sample, which is susceptible to influences from co-existent substances. Background absorbance is also small.

- High sensitivity mode (0. 0H)

  The highest sensitivity can be obtained in this mode but, at the same time, background is higher. This is particularly effective for the measurement of trace elements in city water, ultra-pure water and other samples, which contain small co-existent substances.

  However, the standard mode is better for measurement of the sample, which easily causes background absorption.

This data is measured at the inner gas flow of 0 *l*/min in the atomization mode. Absorbance sensitivity can be controlled by flowing the inner gas (0 to 1.5 *l*/min) in this step. When the inner gas flow is 1.5 *l*/min, absorbance sensitivity drops to about 1/5 and the high concentration calibration curve can be prepared.

## 7.2 Application to actual samples

The temperature program of this data is designed for the standard solution. Good results may not be obtained in the heating condition described here, because matrix components, concentration, and the type and concentration of co-existent substances are different in the actual sample.

Therefore, when a matrix component is contained or the concentrations of co-existent substances are high, the suitable conditions for the actual sample should be set by the method of the analysis condition in the cookbook section 2-2-2 Furnace Analysis Method, based on the heating condition of this data.

### 7.3 Types and life of graphite tube

The following three types of graphite tubes are supplied, and used depending on the element to be measured and the interference level.

- High-density graphite tube

  This can be used for the measurement of most elements and can obtain excellent results in repeatability of the absorption signal. However, with B, Ca, Mo and other metals, which easily react on carbon, the target component does not volatilize completely during atomization and memory effect occurs. With an organic solvent type sample, penetration into the graphite tube increases and sensitivity may drop sharply or memory effect may occur.

- Pyrolytic graphite tube

  A surface treatment is done on the high-density graphite tube to make a pyrolytic tube. Because sample penetration into the tube is small, excellent results can be obtained with an organic solvent type sample. The memory effect hardly occurs with B, Ca, Mo, etc. mentioned above.

  Its absorbance sensitivity is two to three times higher than that of the high-density graphite tube with A*l* and Si and 4b, 5b, 6b, 7b, 8 groups (Ti, V, Cr, Mo, Fe, Co, Ni, Cu, etc.) and lanthanoids in the periodic table of elements.

  Its repeatability of the absorption signal may be worse than that of the high-density graphite tube.

- Platform type graphite tube

  A graphite plate of 1 mm thickness and several mm$^2$ size is set in the graphite tube to make the platform type graphite tube. Because this tube heats the sample indirectly and evenly, interference of co-existent substances and background absorption decrease. This is effective for the analysis of metal samples containing matrix components and elements and in blood or seawater; particularly for analysis of Cd, Pb and other metals, which have low boiling points.

  The graphite tube can be used until it is broken, unless a sensitivity or repeatability drop occurs. This life varies widely depending on liquid properties of the sample to be measured. It can be used 2000 times with the sample, which hardly contains any acid or co-existent substances.

  However, its use may be limited to 300 times with the sample, which has high acid concentration or many co-existent substances.

Therefore, it is recommended to count service times of the graphite tube in measurement and check the tube life for the sample in advance. The AA-6401 or 6501 have the program to count service times of the tube, so this can be used to know the time when the tube should be changed.

### 7.4 Interference, background absorption, and measuring cautions

Cautions for measuring each element and interference are enumerated below.

Some samples may not be measured properly simply by devising the heating program. In such case, good results may be obtained if the matrix modifier is added in accordance with the cookbook section 2-5.3 (Chemical interference and its correction method).

When background absorption correction is done, a sensitivity drop occurs in the BGC-SR method, as compared with BGC-$D_2$ method for the principle reason. If the element being analyzed is at the 430 nm or longer wavelength range, the BGC-SR method should be used for better correction accuracy.

| | |
|---|---|
| Al | Ar gas is used as the gas. When $N_2$ gas exists, strong monocyanide is produced. |
| As | Sensitivity slightly increases by using $N_2$ rather than Ar as the sheath gas. The ashing temperature can be increased by adding $Mg(NO_3)_2$ or $Ni(NO_3)_2$. |
| Ca | Because the graphite tube produces carbide, use of the pyrolytic graphite tube is preferable. Attention must be given to the ambient atmosphere, the regent, and distilled water being used for micro chemical analysis. |
| Cd | Ashing temperature can be increased by adding about 1% $(NH_4)_2$ $HPO_4$. |
| Co | Interference occurs if a halogenide co-exists.<br>The sensitization effect can be expected by adding 0.5% $Fe(NO_3)_2$.2) |
| Cr | Ar gas is preferable as the sheath gas.<br>If a halogenide co-exists, use the pyrolytic graphite tube. Chromium volatilizes even at low temperature settings. It becomes $CrCl_3$ under the co-existence of NaCl. |
| Cu | Interference occurs if a halogenide co-exists.3) It is preferable to decompose it by wet ashing, or add nitric acid, before the drying or ashing condition is set. |
| Fe | It is relatively insusceptible to interferences from other elements. However, attention must be given to Fe impurities in the graphite tube and ambient atmosphere during micro chemical analysis. |
| Ga | It is recommended to use $HNO_3$ to treat a standard or unknown sample. The double sensitization effect can be expected with the mixed solution of $HNO_3 + H_2O_2$.1) |
| K | Attention must be given to distilled water and the ambient atmosphere during micro chemical analysis.<br>It is desirable to narrow the slit width for measurement, because emission from the graphite tube is strong in this wavelength range. |

| | |
|---|---|
| Mg | Ar gas is preferable as the sheath gas. Attention must be given to distilled water and impurities in the reagent. |
| Mn | It is susceptible to interference if a hologenide co-exist. It is expected that the ashing temperature can be increased from 1100 to 1150°C by adding $HNO_3$. |
| Mo | Carbide is produced by carbon from the graphite tube or the sample, and sensitivity drops. Therefore, using the pyrolytic graphite tube is recommended. |
| Na | Attention must be given to the ambient atmosphere, and distilled water during micro chemical analysis. |
| Ni | Volatilization is small even if ashing temperature is set from 900 to 1000°C. |
| Pb | Volatilization increases when ashing temperature is set from 600 to 650°C or higher. |
| Se | It is desired that the ashing temperature is 300°C or lower. It is expected that the ashing temperature be increased from 1000 to 1100°C by adding Cu, Ni and Mo. |
| Si | The use of $N_2$ gas is preferable to Ar as the sheath gas.<br>Using the pyrolytic graphite tube is recommended. |
| Sn | Ar is preferable as the sheath gas, and higher sensitivity can be obtained with a smaller flow. |
| Ti | Sensitivity is low and the atomization temperature is 2700 to 3000°C. The pyrolytic graphite tube is used. |
| V | Volatilization is small even if the ashing temperature is set at 700°C. The use of the pyrolytic graphite tube is preferable. |
| Zn | Attention must be given to the atmosphere and distilled water during micro chemical analysis. The sensitization effect can be obtained by adding Al $(NO_3)_2$.[4] |

## Reference

1) R. D. Ediger, At. Absorpt. Newsl., 14, 127-130 (1975)
"AA Analysis with the Graphite Furnace Using Matrix Modification".

2) R. B. Cruz and J. C. Van Loon, Anal. Chim. Acta, 72, 231-243 (1974)
"A. Critical study of Graphite Furnace Non-Flaml AAS to the Determination of Trace Base Metals in Complex Heavy Matrix Sample Solutions".

3) W. J. Price, Spectrochemical Analysis by Atomic Absorption, HEYDEN.

4) F.J.M. Maesen, J. Balke and R. Massee, Spectrochim.
Acta, 33B, 311-324 (1978)
"Non-Spectral Interferences in Flameless AAS Using Graphite Mini-Tube Furnaces".

# Silver (Ag)

## 7.5 Measuring conditions by element

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

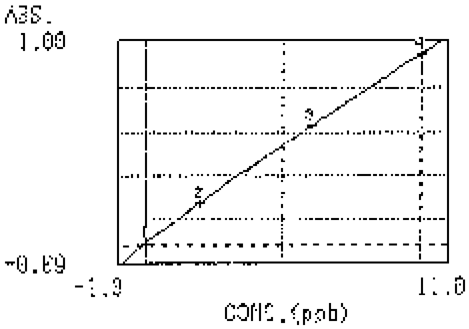
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/400 mA |
| Wavelength | ; 328.1 nm | ; 328.1 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 400 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 400 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

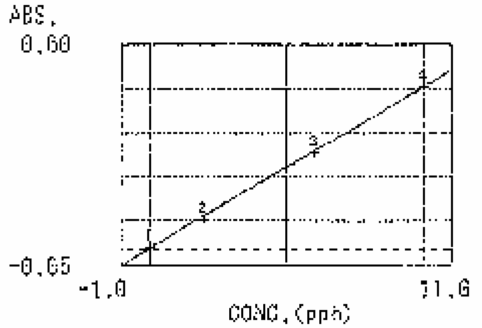
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0039 |
| 2 | 2.0000 | 0.2014 |
| 3 | 6.0000 | 0.5895 |
| 4 | 10.0000 | 0.9301 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999
K0= 0.0016, K1= 0.1043, K2= –0.0011

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0057 |
| 2 | 2.0000 | 0.0868 |
| 3 | 6.0000 | 0.2843 |
| 4 | 10.0000 | 0.4801 |



## Silver (Ag)

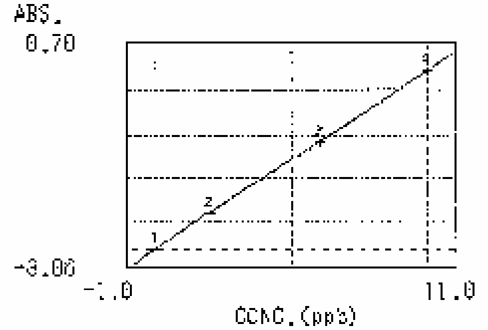
$[ABS]=K1*[C]+K0 \quad r^2=0.9991$
$K0= 0.0012, K1= 0.0479$

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 400 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 400 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

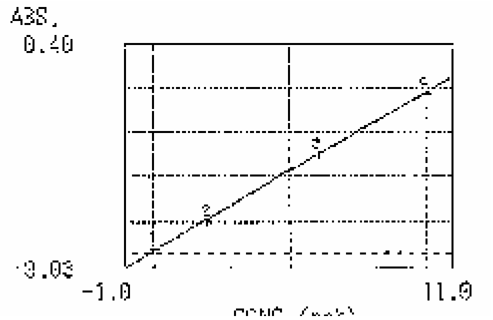
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0033 |
| 2 | 2.0000 | 0.1217 |
| 3 | 6.0000 | 0.3734 |
| 4 | 10.0000 | 0.6077 |



$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9999$
$K0= 0.0010, K1= 0.0629, K2= –0.0002$

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>328.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0062 |
| 2 | 2.0000 | 0.0572 |
| 3 | 6.0000 | 0.1828 |
| 4 | 10.0000 | 0.3060 |



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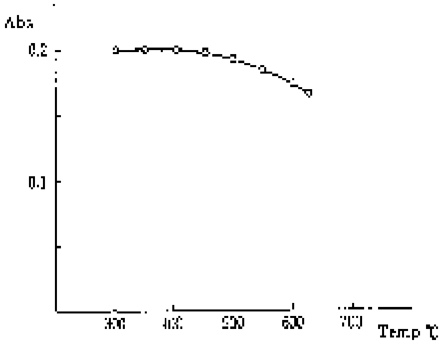
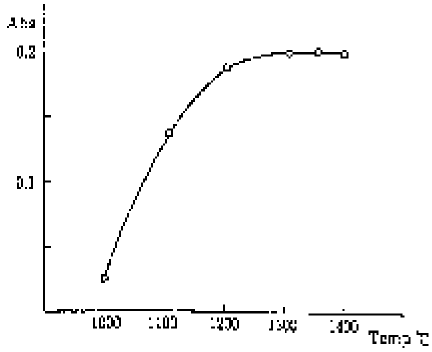




## Aluminum (A*l*)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

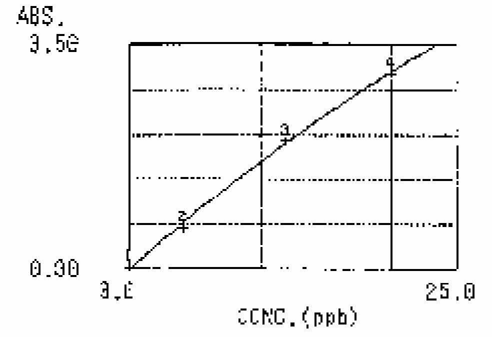
| | | |
|---|---|---|
| Current | ; 8 mA/0 mA | ; 10 mA/600 mA |
| Wavelength | ; 309.3 nm | ; 309.3 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0035 |
| 2 | 4.0000 | 0.0896 |
| 3 | 12.0000 | 0.2846 |
| 4 | 20.0000 | 0.4353 |

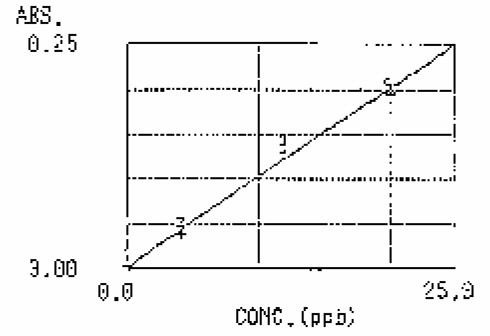


$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9989$

K0= 0.0010, K1= 0.0255, K2= –0.0002

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0028 |
| 2 | 4.0000 | 0.0381 |
| 3 | 12.0000 | 0.1298 |
| 4 | 20.0000 | 0.1950 |



$[ABS]=K1*[C]+K0 \quad r^2=0.9949$

K0= 0.0030, K1= 0.0098

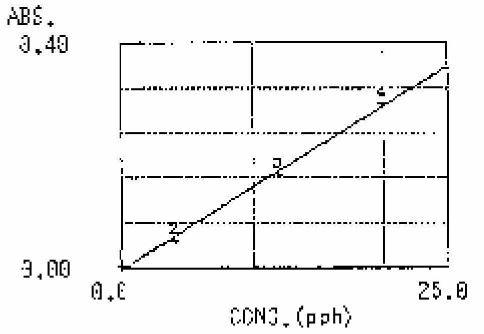
## Aluminum (A*l*)

- Graphite furnace temperature program (Standard mode 0. 0), pyrolytic graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0035 |
| 2 | 4.0000 | 0.0497 |
| 3 | 12.0000 | 0.1653 |
| 4 | 20.0000 | 0.2914 |

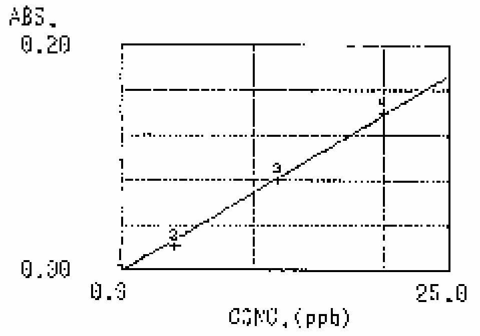


[ABS]=K1*[C]+K0 $r^2$=0.9975

K0= –0.0030, K1= 0.0145

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>309.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0037 |
| 2 | 4.0000 | 0.0219 |
| 3 | 12.0000 | 0.0802 |
| 4 | 20.0000 | 0.1399 |

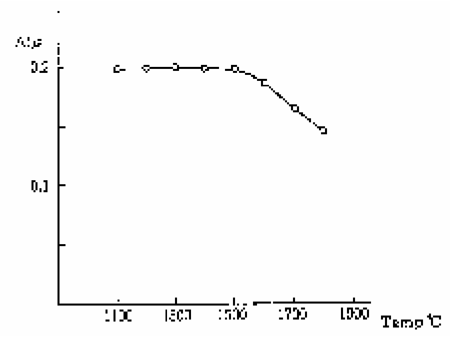


[

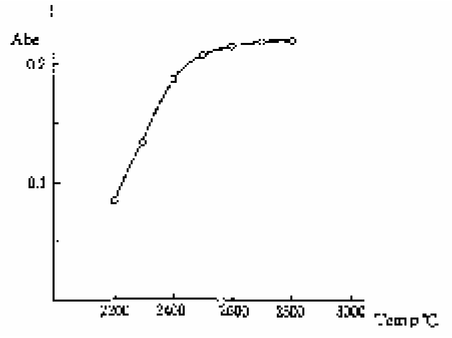
K0= 0.0010, K1= 0.0069

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l* Metal)

Ashing condition



Atomization condition



## Arsenic (As)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Measuring conditions

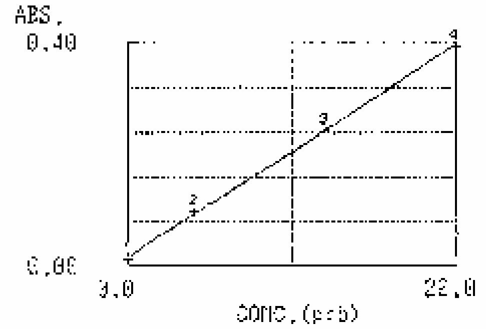
| | | |
|---|---|---|
| Current | ; 12 mA/0 mA | ; 12 mA/500 mA |
| Wavelength | ; 193.7 nm | ; 193.7 nm |
| Slit width | ; 0.5 nm | ; 2.0 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), high density graphite tube, Pd 10 ppm added

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

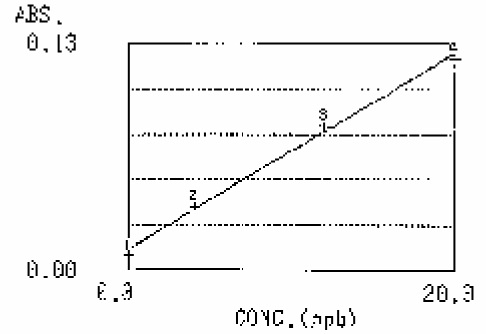
| STD. No. | CONC. (ppb) | ABS. 193.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0113 |
| 2 | 4.0000 | 0.0996 |
| 3 | 12.0000 | 0.2456 |
| 4 | 20.0000 | 0.3922 |



[ABS]=K1*[C]+K0 $r^2$=0.9989
K0= 0.0174, K1= 0.0189

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD. No. | CONC. (ppb) | ABS. 193.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0085 |
| 2 | 4.0000 | 0.0366 |
| 3 | 12.0000 | 0.0838 |
| 4 | 20.0000 | 0.1219 |



[ABS]=K1*[C]+K0 $r^2$=0.9945
K0= 0.0119, K1= 0.0056

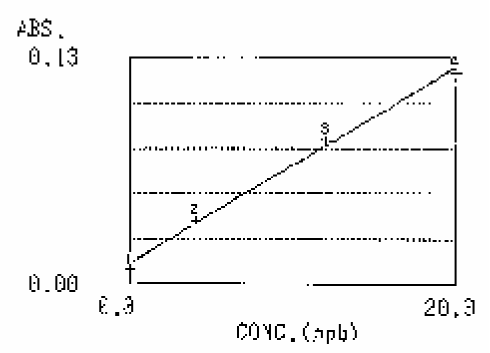
## Arsenic (As)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube, Pd 10 ppm added

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 93.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0158 |
| 2 | 4.0000 | 0.0569 |
| 3 | 12.0000 | 0.1534 |
| 4 | 20.0000 | 0.2412 |

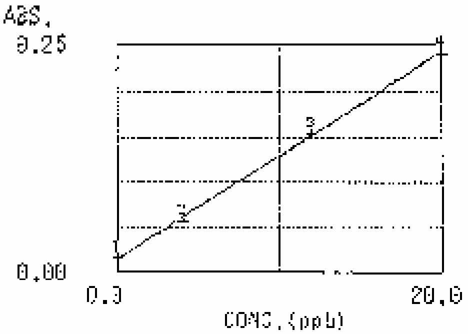


[ABS]=K1*[C]+K0  $r^2$=0.9994

K0= 0.0114, K1= 0.0114

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 193.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0120 |
| 2 | 4.0000 | 0.0243 |
| 3 | 12.0000 | 0.0476 |
| 4 | 20.0000 | 0.0750 |

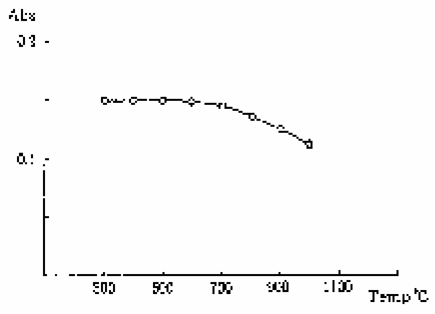


[ABS]=K1*[C]+K0  $r^2$=0.9987

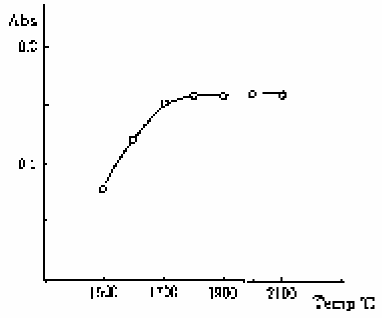
K0= 0.0116, K1= 0.0031

- Ashing temperature, atomization temperature and sensitivity (Solution: NaOH, $As_2O_3$)

Ashing condition



Atomization condition



# Gold (Au)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

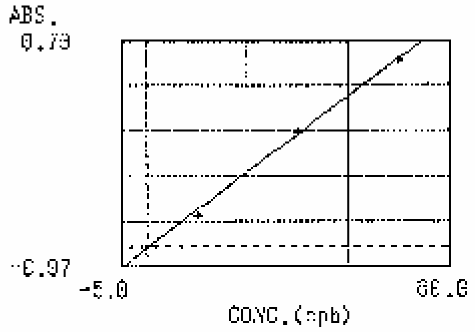
| | | |
|---|---|---|
| Current | ; 12 mA/0 mA | ; 10 mA/400 mA |
| Wavelength | ; 242.8 nm | ; 242.8 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1700 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0023 |
| 2 | 10.0000 | 0.1088 |
| 3 | 30.0000 | 0.3908 |
| 4 | 50.0000 | 0.6341 |

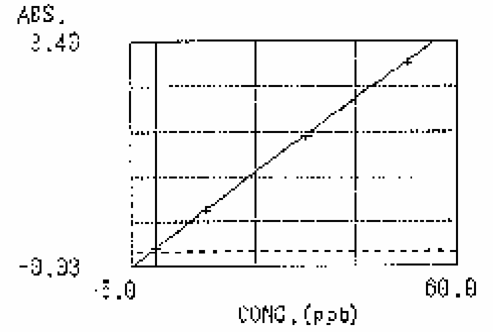


$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9984$

K0= –0.0056, K1= 0.0129, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0061 |
| 2 | 10.0000 | 0.0796 |
| 3 | 30.0000 | 0.2228 |
| 4 | 50.0000 | 0.3609 |



$[ABS]=K2*[C]^2+K1*[C]+KO$  $r^2=1.0000$

K0= 0.0061, K1= 0.0074, K2= –0.0000

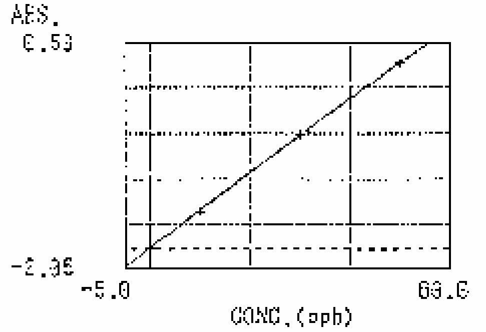
## Gold (Au)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1700 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-D$_2$ mode (Sample injection volume 20 μ*l*)

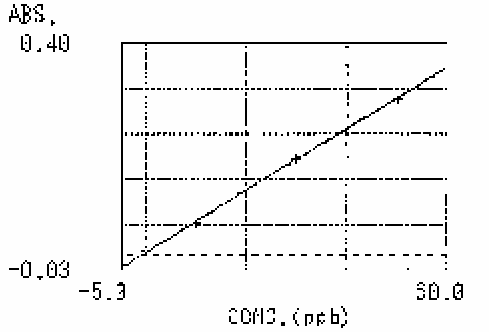
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0029 |
| 2 | 10.0000 | 0.0922 |
| 3 | 30.0000 | 0.2784 |
| 4 | 50.0000 | 0.4494 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9999
K0= 0.0013, K1= 0.0095, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

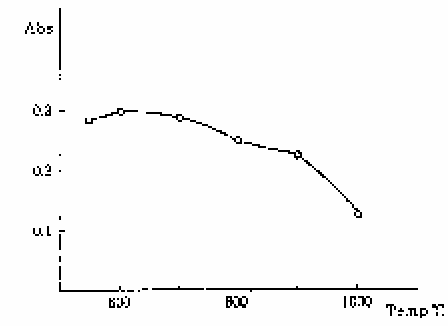
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>242.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0073 |
| 2 | 10.0000 | 0.0600 |
| 3 | 30.0000 | 0.1820 |
| 4 | 50.0000 | 0.2959 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9996
K0= 0.0055, K1= 0.0058, K2= 0.000

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition

# Beryllium (Be)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

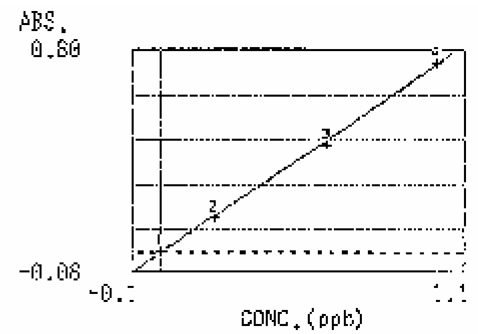
Current ; 16 mA/0 mA
Wavelength ; 234.9 nm
Slit width ; 0.5 nm
Lighting mode ; BGC-$D_2$

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 234.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0041 |
| 2 | 0.2000 | 0.1367 |
| 3 | 0.6000 | 0.4307 |
| 4 | 1.0000 | 0.7463 |



[ABS]=K1*[C]+K0  $r^2$=0.9991
K0= 0.0054, K1= 0.7441

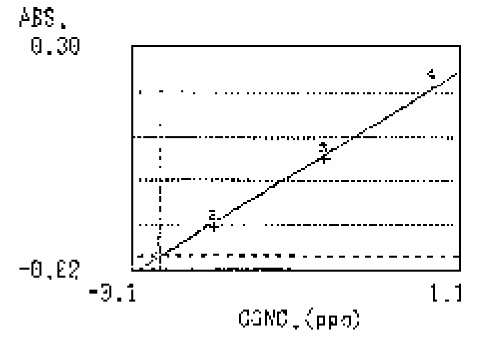
## Beryllium (Be)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>234.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0041 |
| 2 | 0.2000 | 0.0412 |
| 3 | 0.6000 | 0.1389 |
| 4 | 1.0000 | 0.2434 |



[ABS]=K1*[C]+K0  $r^2$=0.9973

K0= 0.0019 K1= 0.2416

# Bismuth (Bi)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

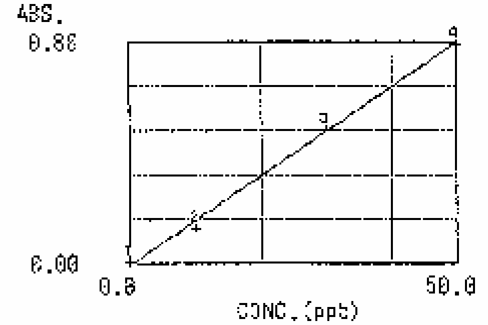
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/300 mA |
| Wavelength | ; 223.1 nm | ; 223.1 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 450 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 450 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1700 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

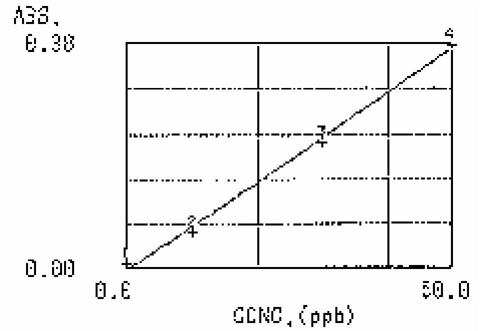
| STD. No. | CONC. (ppb) | ABS. 223.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0069 |
| 2 | 10.0000 | 0.1326 |
| 3 | 30.0000 | 0.4847 |
| 4 | 50.0000 | 0.7950 |



[ABS]=K1*[C]+K0 $r^2$=0.9981
K0= –0.0065, K1= 0.0161

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 223.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0072 |
| 2 | 10.0000 | 0.0624 |
| 3 | 30.0000 | 0.2143 |
| 4 | 50.0000 | 0.3764 |



[ABS]=K1*[C]+K0 $r^2$=0.9967
K0= 0.0030, K1= 0.0075

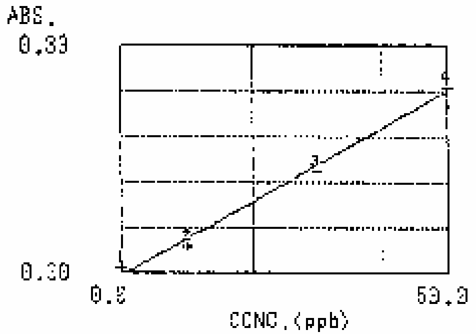
## Bismuth (Bi)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 450 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 450 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1700 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 223.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0080 |
| 2 | 10.0000 | 0.0358 |
| 3 | 30.0000 | 0.1334 |
| 4 | 50.0000 | 0.2464 |

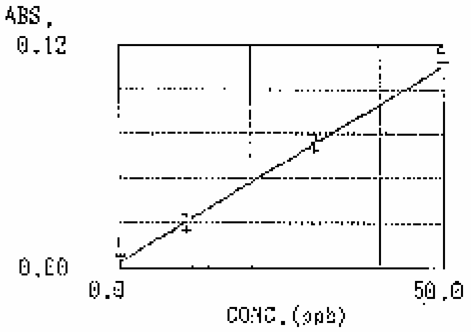


$[ABS]=K1*[C]+K0 \quad r^2=0.9901$

K0= –0.0032, K1= 0.0048

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 223.1nm |
|---|---|---|
| 1 | 0.0000 | 0.0071 |
| 2 | 10.0000 | 0.0205 |
| 3 | 30.0000 | 0.0637 |
| 4 | 50.0000 | 0.1107 |

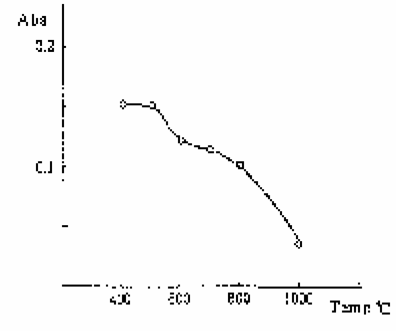


$[ABS]=K1*[C]+K0 \quad r^2=0.9938$

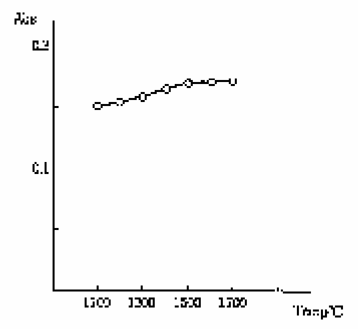
K0= 0.0031, K1= 0.0021

- Ashing temperature, atomization temperature and sensitivity (Solution: $HNO_3$, Metal)

Ashing condition



Atomization condition



## Calcium (Ca)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

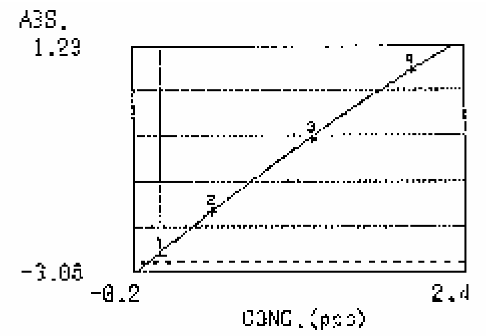
Current ; 10 mA/0 mA
Wavelength ; 422.7 nm
Slit width ; 0.5 nm
Lighting mode ; BGC-$D_2$

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 422.7nm |
| 1 | 0.0000 | 0.0438 |
| 2 | 0.4000 | 0.2778 |
| 3 | 1.2000 | 0.6807 |
| 4 | 2.0000 | 1.0625 |



$$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9998$$

K0= 0.0477, K1= 0.5690, K2= –0.0312

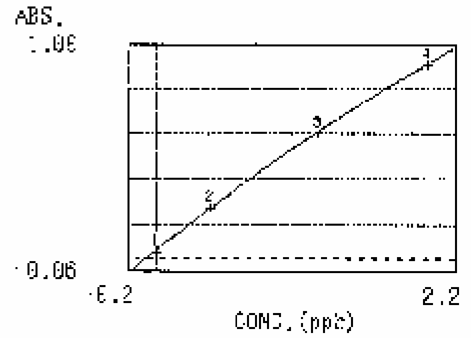
## Calcium (Ca)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

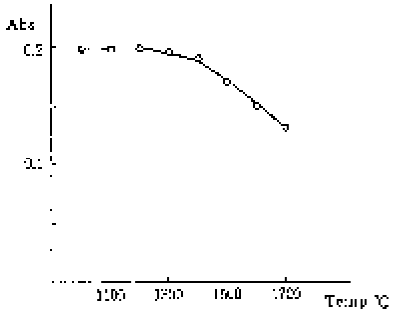
| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 422.7nm |
| 1 | 0.0000 | 0.0302 |
| 2 | 0.4000 | 0.2305 |
| 3 | 1.2000 | 0.5795 |
| 4 | 2.0000 | 0.9083 |

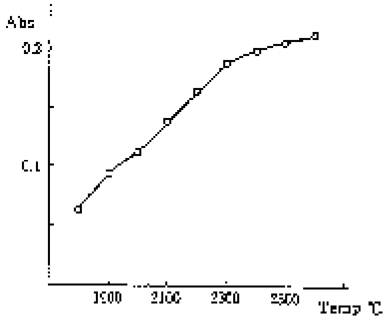


$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9999$

K0= 0.0331, K1= 0.4904, K2= –0.0267

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, $CaCO_3$)


Ashing condition


Atomization condition

# Cadmium (Cd)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

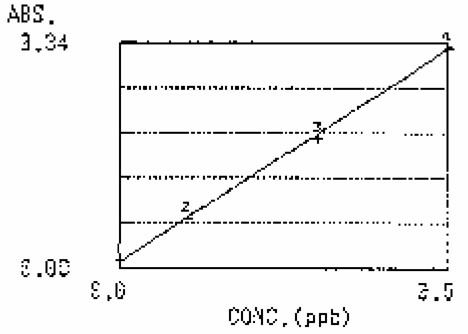
| | | |
|---|---|---|
| Current | ; 8 mA/0 mA | ; 8 mA/300 mA |
| Wavelength | ; 228.8 nm | ; 228.8 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

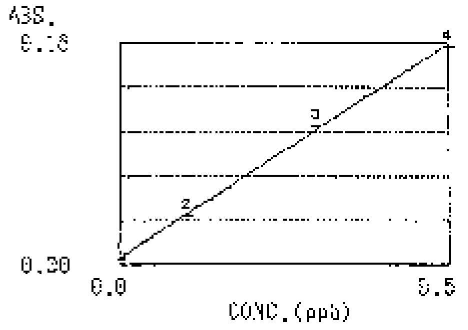
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>228.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0129 |
| 2 | 0.1000 | 0.0751 |
| 3 | 0.3000 | 0.1971 |
| 4 | 0.5000 | 0.3340 |



[ABS]=K1*[C]+K0 $r^2$=0.9992
K0= –0.0109, K1= 0.6395

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>228.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0047 |
| 2 | 0.1000 | 0.0363 |
| 3 | 0.3000 | 0.1005 |
| 4 | 0.5000 | 0.1577 |



[ABS]=K1*[C]+K0 $r^2$=0.9993
K0= 0.0057, K1= 0.3072

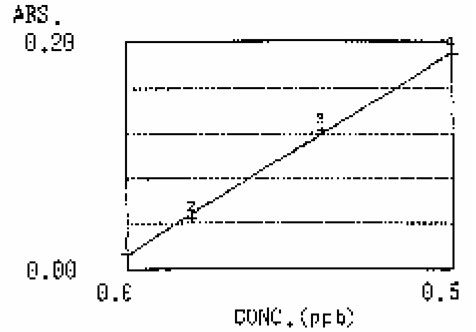
## Cadmium (Cd)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

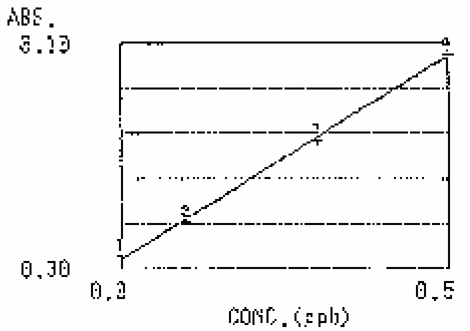
| STD. No. | CONC. (ppb) | ABS. 228.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0138 |
| 2 | 0.1000 | 0.0453 |
| 3 | 0.3000 | 0.1224 |
| 4 | 0.5000 | 0.1894 |



[ABS]=K1*[C]+K0  $r^2$=0.9989
K0= –0.0127, K1= 0.3558

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

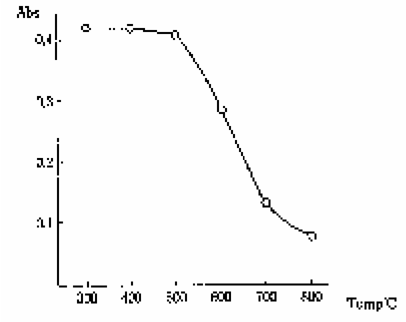
| STD. No. | CONC. (ppb) | ABS. 228.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0060 |
| 2 | 0.1000 | 0.0211 |
| 3 | 0.3000 | 0.0568 |
| 4 | 0.5000 | 0.0951 |



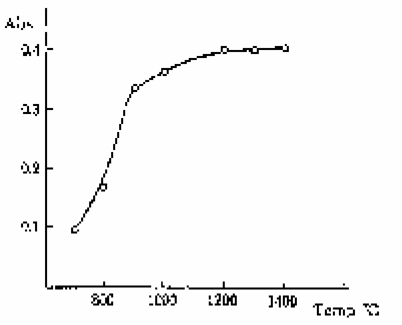
[ABS]=K1*[C]+K0  $r^2$=0.9985
K0= 0.0045, K1= 0.1791

- Ashing temperature, atomization temperature and sensitivity (Solution: $HNO_3$, Metal)

Ashing condition



Atomization condition



## Chromium (Cr)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

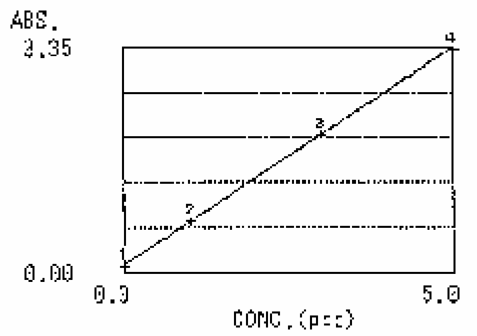
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/600 mA |
| Wavelength | ; 357.9 nm | ; 357.9 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 10 $\mu l$)

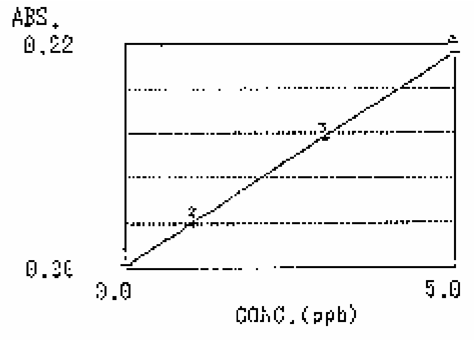
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>357.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0108 |
| 2 | 1.0000 | 0.0807 |
| 3 | 3.0000 | 0.2158 |
| 4 | 5.0000 | 0.3478 |



[ABS]=K1*[C]+K0 $r^2$=0.9999
K0= 0.0123, K1= 0.0673

- Calibration curve in BGC-SR mode (Sample injection volume 10 $\mu l$)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>357.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0043 |
| 2 | 1.0000 | 0.0444 |
| 3 | 3.0000 | 0.1268 |
| 4 | 5.0000 | 0.2121 |



[ABS]=K1*[C]+K0 $r^2$=0.9999
K0= 0.0034, K1= 0.0416

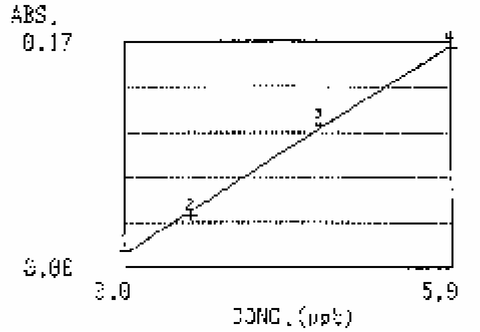
## Chromium (Cr)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 10 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 357.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0124 |
| 2 | 1.0000 | 0.0389 |
| 3 | 3.0000 | 0.1078 |
| 4 | 5.0000 | 0.1661 |

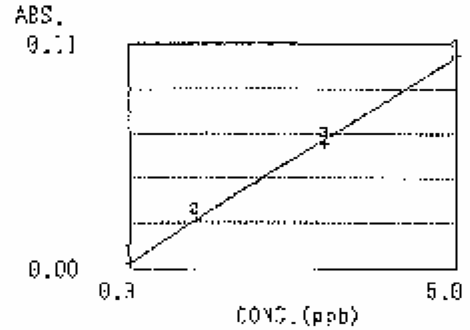


[ABS]=K1*[C]+K0  $r^2$=0.9983

K0= –0.0110, K1= 0.0313

- Calibration curve in BGC-SR mode (Sample injection volume 10 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 357.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0031 |
| 2 | 1.0000 | 0.0236 |
| 3 | 3.0000 | 0.0617 |
| 4 | 5.0000 | 0.1042 |

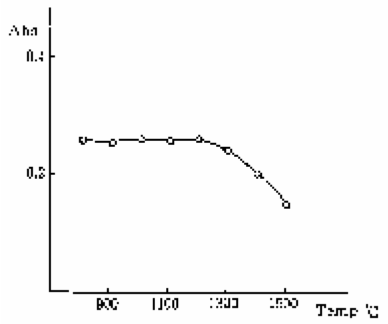


[ABS]=K1*[C]+K0  $r^2$=0.9994

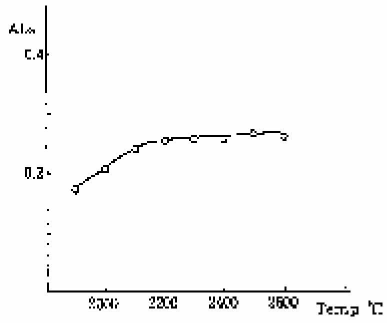
K0= 0.0029, K1= 0.0201

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, Metal)

Ashing condition



Atomization condition



# Cobalt (Co)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

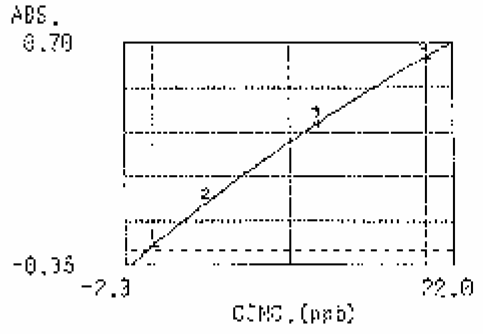
| | | |
|---|---|---|
| Current | ; 12 mA/0 mA | ; 12 mA/400 mA |
| Wavelength | ; 240.7 nm | ; 240.7 nm |
| Slit width | ; 0.2 nm | ; 0.2 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 400 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 400 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20µl)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 240.7nm |
| 1 | 0.0000 | 0.0169 |
| 2 | 4.0000 | 0.1578 |
| 3 | 12.0000 | 0.4332 |
| 4 | 20.0000 | 0.6482 |

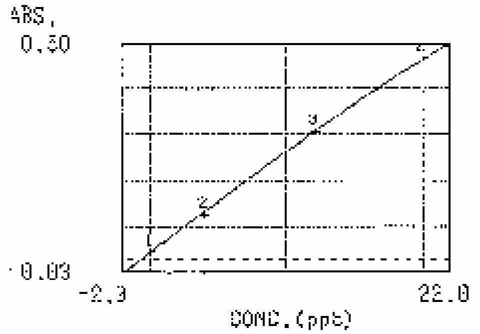


[ABS]=K2*[C]$^2$+K1*[C]+K0   $r^2$=0.9997

K0= 0.0138, K1= 0.0389, K2= –0.0004

- Calibration curve in BGC-SR mode (Sample injection volume 20 µl)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 240.7nm |
| 1 | 0.0000 | 0.0178 |
| 2 | 4.0000 | 0.1058 |
| 3 | 12.0000 | 0.2953 |
| 4 | 20.0000 | 0.4600 |



[ABS]=K2*[C]$^2$+K1*[C]+K0   $r^2$=0.9997

K0= 0.0152, K1= 0.0243, K2= –0.0000

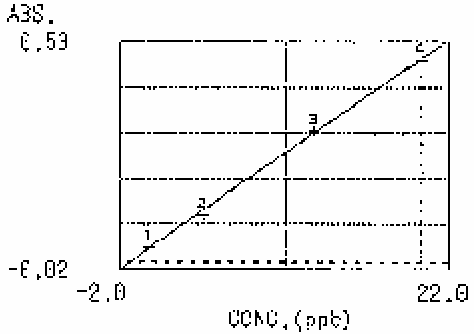
# Cobalt (Co)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 400 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 400 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 240.7nm |
| 1 | 0.0000 | 0.0319 |
| 2 | 4.0000 | 0.1063 |
| 3 | 12.0000 | 0.2988 |
| 4 | 20.0000 | 0.4591 |

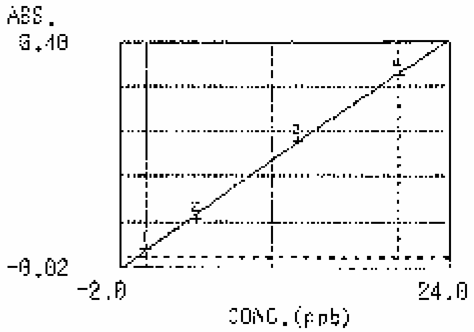


[ABS]=K2*[C]$^2$+K1*[C]+K0   $r^2$=0.9983

K0= 0.0265, K1= 0.0227, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 240.7nm |
| 1 | 0.0000 | 0.0154 |
| 2 | 4.0000 | 0.0715 |
| 3 | 12.0000 | 0.2148 |
| 4 | 20.0000 | 0.3384 |

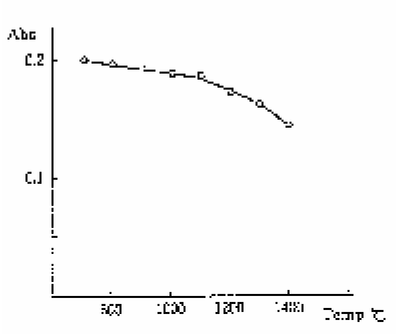


[ABS]=K2*[C]$^2$+K1*[C]+K0   $r^2$=0.9987

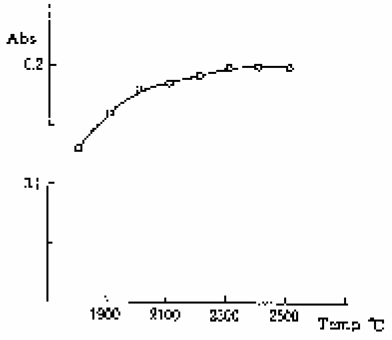
K0= 0.0117, K1= 0.0167, K2= –0.0000

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, CoC*l*)

Ashing condition



Atomization condition



# Copper (Cu)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

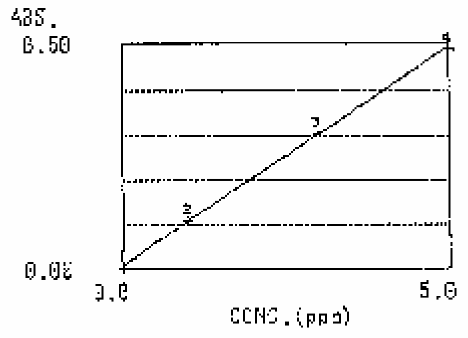
| | | |
|---|---|---|
| Current | ; 6 mA/0 mA | ; 10 mA/500 mA |
| Wavelength | ; 324.8 nm | ; 324.8 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

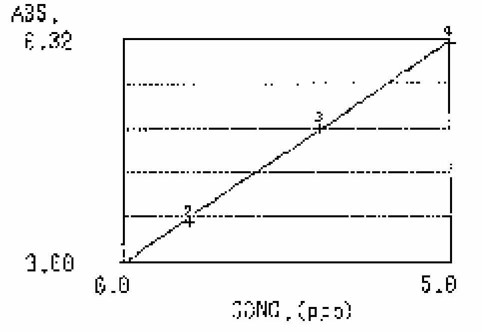
| STD. No. | CONC. (ppb) | ABS. 324.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0041 |
| 2 | 1.0000 | 0.1062 |
| 3 | 3.0000 | 0.3052 |
| 4 | 5.0000 | 0.4881 |



[ABS]=K1*[C]+K0 $r^2$=0.9994
K0= 0.0079, K1= 0.0969

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 324.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0025 |
| 2 | 1.0000 | 0.0564 |
| 3 | 3.0000 | 0.1937 |
| 4 | 5.0000 | 0.3153 |



[ABS]=K1*[C]+K0 $r^2$=0.9988
K0= –0.0008, K1= 0.0635

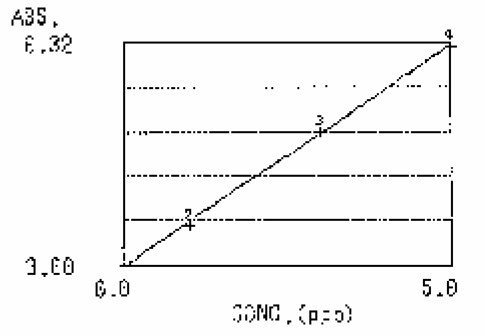
## Copper (Cu)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

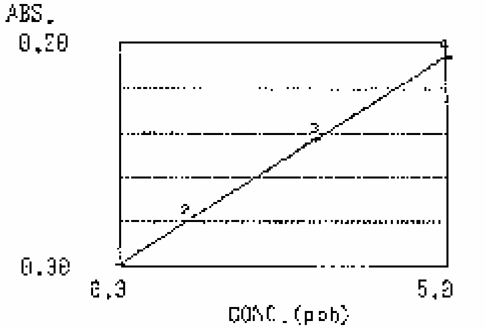
| STD. No. | CONC. (ppb) | ABS. 324.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0046 |
| 2 | 1.0000 | 0.0692 |
| 3 | 3.0000 | 0.1883 |
| 4 | 5.0000 | 0.3104 |



[ABS]=K1*[C]+K0  $r^2$=0.9999
K0= 0.0061, K1= 0.0609

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

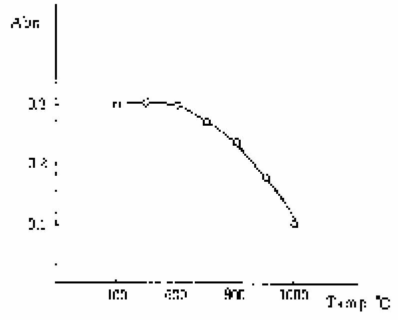
| STD. No. | CONC. (ppb) | ABS. 324.8nm |
|---|---|---|
| 1 | 0.0000 | 0.0027 |
| 2 | 1.0000 | 0.0403 |
| 3 | 3.0000 | 0.1148 |
| 4 | 5.0000 | 0.1887 |



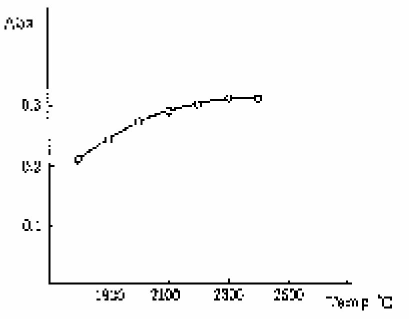
[ABS]=K1*[C]+K0  $r^2$=1.0000
K0= 0.0030, K1= 0.0372

- Ashing temperature, atomization temperature and sensitivity (Solution: $HNO_3$, Metal)

Ashing condition



Atomization condition



## Iron (Fe)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

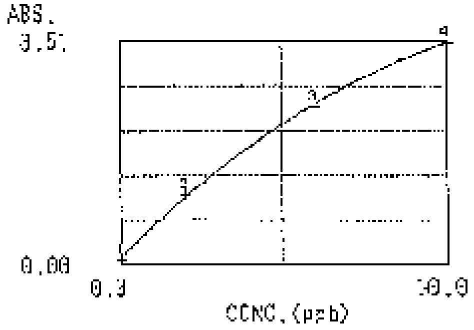
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/400 mA |
| Wavelength | ; 248.3 nm | ; 248.3 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 248.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0128 |
| 2 | 2.0000 | 0.1604 |
| 3 | 6.0000 | 0.3616 |
| 4 | 10.0000 | 0.5061 |

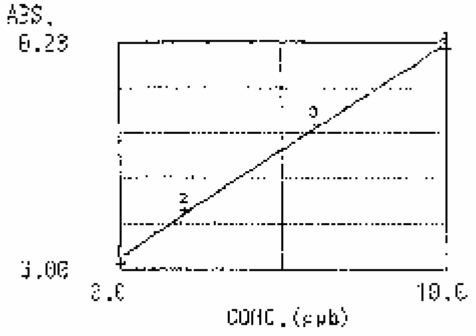


[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9993

K0= 0.0169, K1= 0.0726, K2= –0.0024

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 248.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0081 |
| 2 | 2.0000 | 0.0722 |
| 3 | 6.0000 | 0.1792 |
| 4 | 10.0000 | 0.2736 |



[ABS]=K1*[C]+K0  $r^2$=0.9969

K0= 0.0146, K1= 0.0264

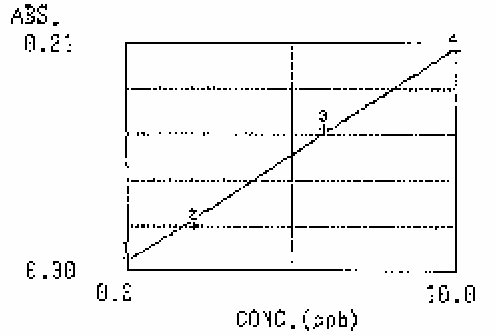
## Iron (Fe)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>248.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0113 |
| 2 | 2.0000 | 0.0427 |
| 3 | 6.0000 | 0.1322 |
| 4 | 10.0000 | 0.2032 |

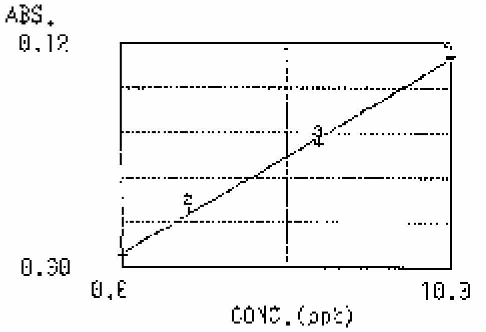


[ABS]=K1*[C]+K0  $r^2$=0.9969

K0= 0.0090, K1= 0.0196

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>248.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0069 |
| 2 | 2.0000 | 0.0301 |
| 3 | 6.0000 | 0.0671 |
| 4 | 10.0000 | 0.1120 |

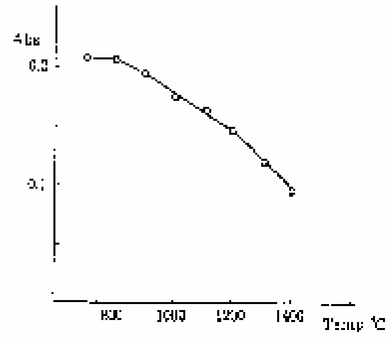


[ABS]=K1*[C]+K0  $r^2$=0.9982

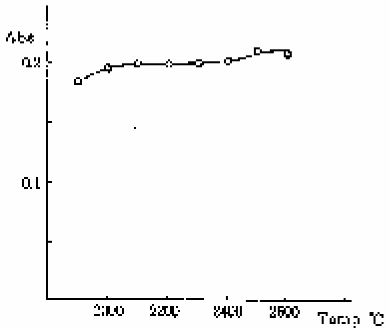
K0= 0.0074, K1= 0.0104

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



## Potassium (K)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

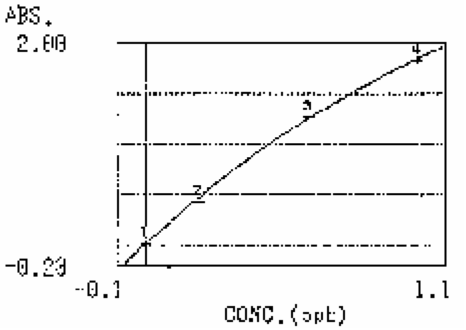
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 8 mA/600 mA |
| Wavelength | ; 766.5 nm | ; 766.5 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; HCL | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 $\mu l$)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>766.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0291 |
| 2 | 0.2000 | 0.4344 |
| 3 | 0.6000 | 1.2729 |
| 4 | 1.0000 | 1.8376 |

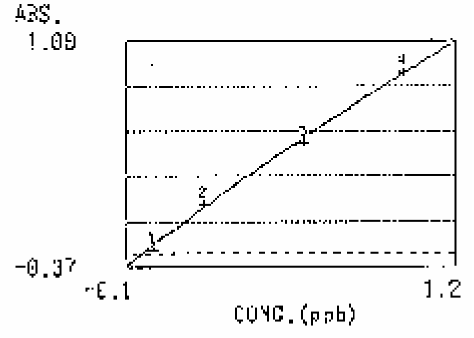


[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=0.9989

K0= –0.0103, K1= 2.4115, K2= –0.5771

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>766.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0165 |
| 2 | 0.2000 | 0.2293 |
| 3 | 0.6000 | 0.5208 |
| 4 | 1.0000 | 0.8520 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=0.9973

K0= 0.0297, K1= 0.8889, K2= –0.0715

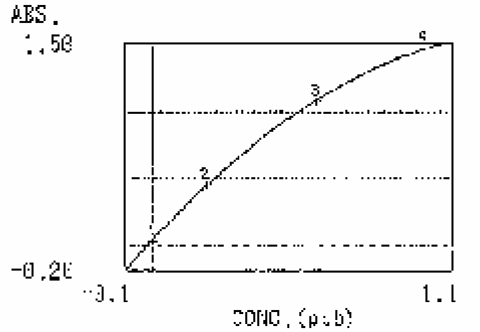
## Potassium (K)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

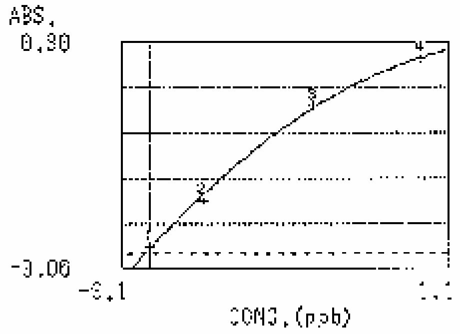
| STD. No. | CONC. (ppb) | ABS. 766.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0288 |
| 2 | 0.2000 | 0.4530 |
| 3 | 0.6000 | 1.0776 |
| 4 | 1.0000 | 1.4631 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9999
K0= 0.0323, K1= 2.2299, K2= –0.8005

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

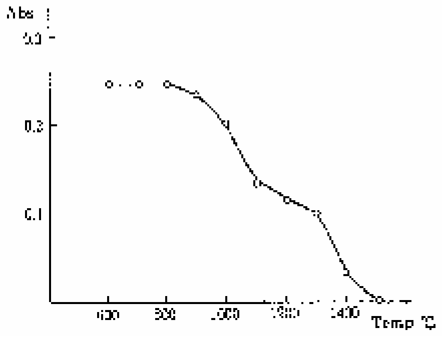
| STD. No. | CONC. (ppb) | ABS. 766.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0216 |
| 2 | 0.2000 | 0.2048 |
| 3 | 0.6000 | 0.5586 |
| 4 | 1.0000 | 0.7381 |



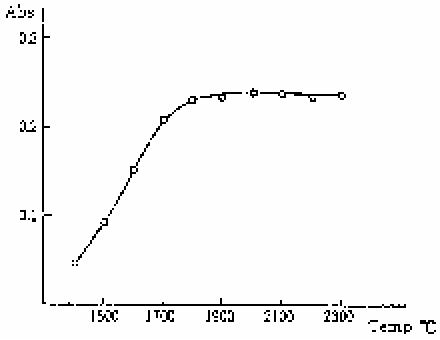
[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9983
K0= 0.0121, K1= 1.1333, K2= –0.4038

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqueous solution, KCl)

Ashing condition



Atomization condition



# Lithium (Li)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

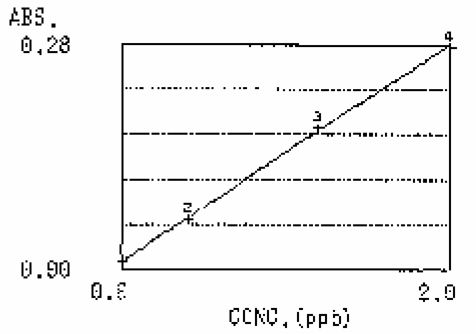
Current ; 8 mA/0 mA
Wavelength ; 670.7 nm
Slit width ; 0.5 nm
Lighting mode ; HCL

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>670.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0104 |
| 2 | 0.4000 | 0.0626 |
| 3 | 1.2000 | 0.1759 |
| 4 | 2.0000 | 0.2793 |



$[ABS]=K1*[C]+K0 \quad r^2=0.9996$

K0= 0.0103, K1= 0.1353

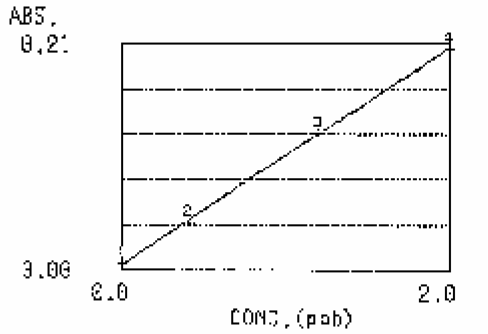
## Lithium (Li)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 670.7nm |
| 1 | 0.0000 | 0.0078 |
| 2 | 0.2000 | 0.0444 |
| 3 | 0.6000 | 0.1276 |
| 4 | 1.0000 | 0.2065 |



[ABS]=K1*[C]+K0  $r^2$=0.9997
K0= 0.0065 K1= 0.1001

# Magnesium (Mg)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

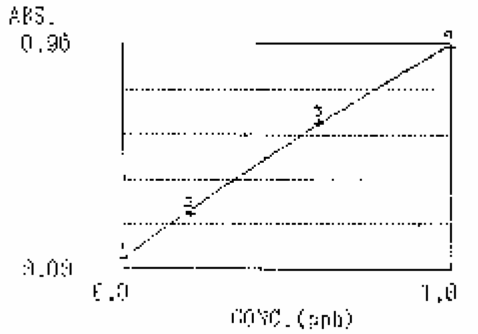
| | | |
|---|---|---|
| Current | ; 8 mA/0 mA | ; 8 mA/500 mA |
| Wavelength | ; 285.2 nm | ; 285.2 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BRG-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2000 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 285.2nm |
| 1 | 0.0000 | 0.0493 |
| 2 | 0.2000 | 0.2389 |
| 3 | 0.6000 | 0.6305 |
| 4 | 1.0000 | 0.9533 |

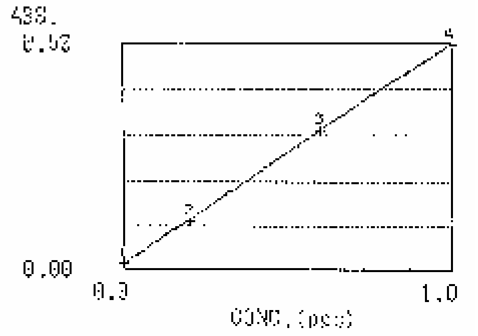


[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9997

K0= –0.0442, K1= 1.0496, K2= –0.1386

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 285.2nm |
| 1 | 0.0000 | 0.0124 |
| 2 | 0.2000 | 0.1088 |
| 3 | 0.6000 | 0.3111 |
| 4 | 1.0000 | 0.4958 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999

K0= 0.0106, K1= 0.5138, K2= –0.0279

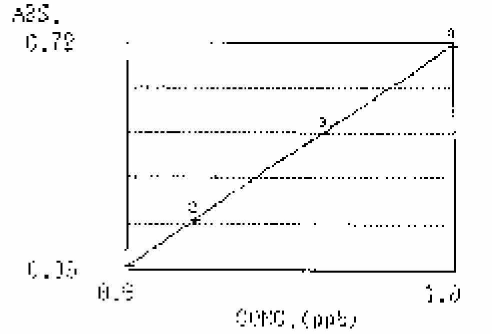
## Magnesium (Mg)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2000 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

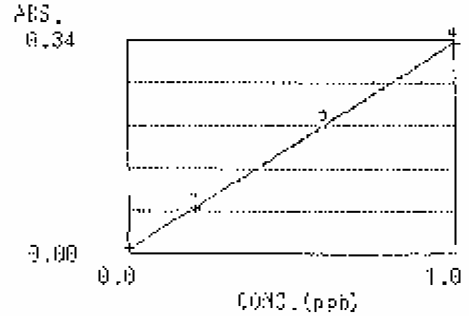
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>285.2nm |
|---|---|---|
| 1 | 0.0000 | 0.0128 |
| 2 | 0.2000 | 0.1564 |
| 3 | 0.6000 | 0.4347 |
| 4 | 1.0000 | 0.7126 |



[ABS]=K1*[C]+K0  $r^2$=1.0000
K0= 0.0147, K1= 0.6988

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

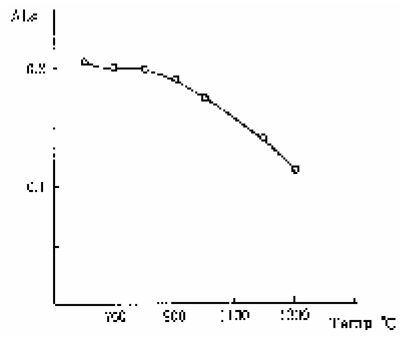
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>285.2nm |
|---|---|---|
| 1 | 0.0000 | 0.0077 |
| 2 | 0.2000 | 0.0732 |
| 3 | 0.6000 | 0.2040 |
| 4 | 1.0000 | 0.3359 |



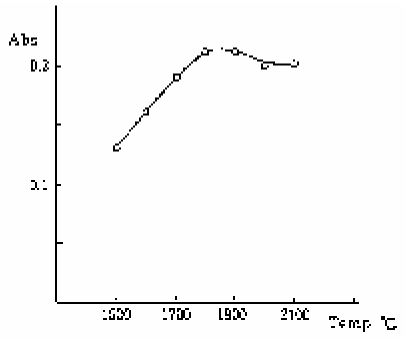
[ABS]=K1*[C]+K0  $r^2$=1.0000
K0= 0.0076, K1= 0.3280

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, Metal)

Ashing condition



Atomization condition



## Manganese (Mn)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

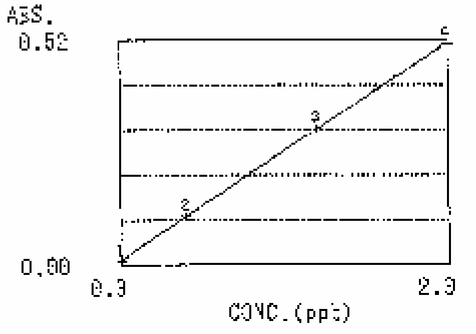
| | | | | |
|---|---|---|---|---|
| Current | ; | 10 mA/0 mA | ; | 10 mA/600 mA |
| Wavelength | ; | 279.5 nm | ; | 279.5 nm |
| Slit width | ; | 0.2 nm | ; | 0.2 nm |
| Lighting mode | ; | BGC-$D_2$ | ; | BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

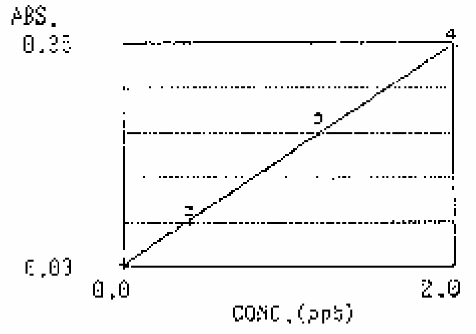
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0097 |
| 2 | 0.4000 | 0.1138 |
| 3 | 1.2000 | 0.3167 |
| 4 | 2.0000 | 0.5117 |



[ABS]=K1*[C]+K0  $r^2$=0.9998
K0= 0.0121, K1= 0.2509

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0052 |
| 2 | 0.4000 | 0.0715 |
| 3 | 1.2000 | 0.2140 |
| 4 | 2.0000 | 0.3450 |



[ABS]=K1*[C]+K0  $r^2$=0.9997
K0= 0.0052, K1= 0.1709

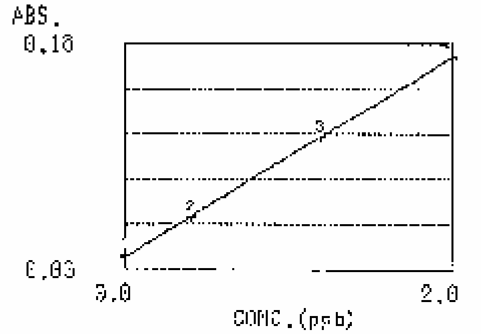
## Manganese (Mn)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

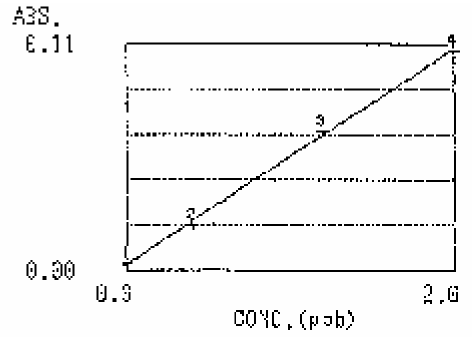
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0102 |
| 2 | 0.4000 | 0.0366 |
| 3 | 1.2000 | 0.0938 |
| 4 | 2.0000 | 0.1505 |



[ABS]=K1*[C]+K0  $r^2$=0.9999
K0= 0.0094, K1= 0.0704

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

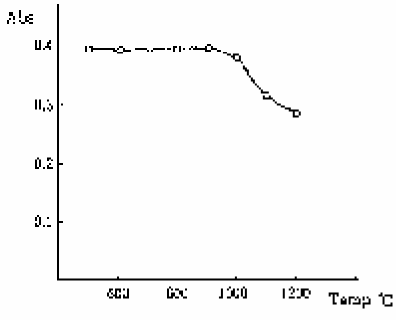
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>279.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0035 |
| 2 | 0.4000 | 0.0217 |
| 3 | 1.2000 | 0.0678 |
| 4 | 2.0000 | 0.1065 |



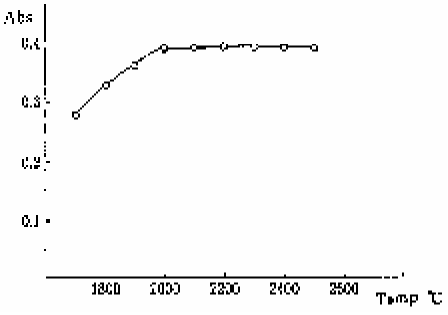
[ABS]=K1*[C]+K0  $r^2$=0.9984
K0= 0.0028, K1= 0.0523

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



# Molybdenum (Mo)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

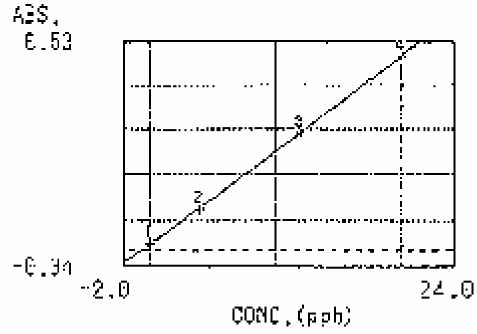
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 10 mA/500 mA |
| Wavelength | ; 313.3 nm | ; 313.3 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

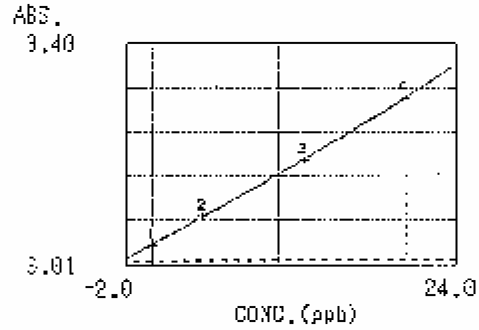
| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 313.3nm |
| 1 | 0.0000 | 0.0145 |
| 2 | 4.0000 | 0.0952 |
| 3 | 12.0000 | 0.2763 |
| 4 | 20.0000 | 0.4645 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999
K0= 0.0133, K1= 0.206, K2= 0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 313.3nm |
| 1 | 0.0000 | 0.0275 |
| 2 | 4.0000 | 0.0795 |
| 3 | 12.0000 | 0.1838 |
| 4 | 20.0000 | 0.2999 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9999
K0= 0.0282, K1= 0.0122, K2= 0.0000

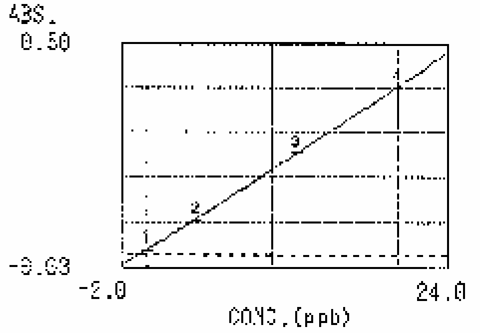
## Molybdenum (Mo)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

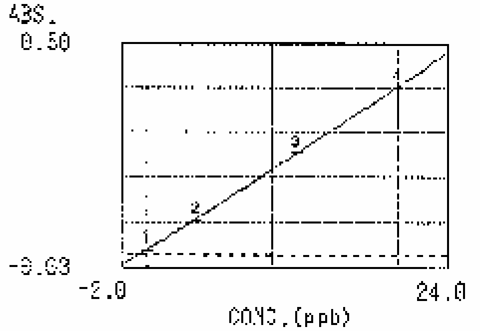
| STD. No. | CONC. (ppb) | ABS. 313.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0141 |
| 2 | 4.0000 | 0.0819 |
| 3 | 12.0000 | 0.2400 |
| 4 | 20.0000 | 0.3972 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9998$
K0= 0.0122, K1= 0.0181, K2= 0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

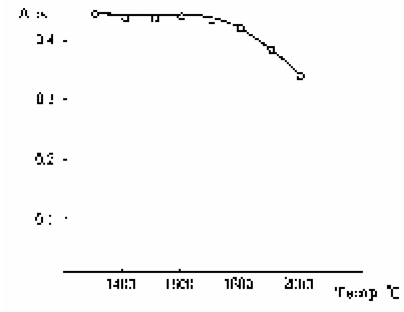
| STD. No. | CONC. (ppb) | ABS. 313.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0245 |
| 2 | 4.0000 | 0.0595 |
| 3 | 12.0000 | 0.1408 |
| 4 | 20.0000 | 0.2196 |



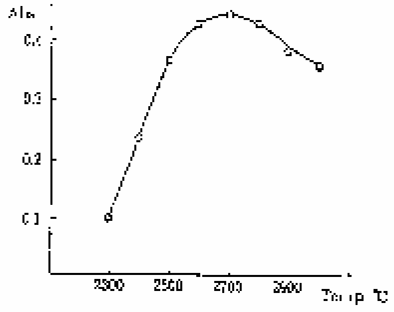
$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9997$
K0= 0.0235, K1= 0.0094, K2= 0.0000

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



# Sodium (Na)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

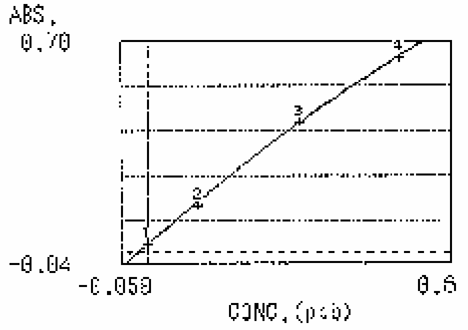
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 8 mA/600 mA |
| Wavelength | ; 589.0 nm | ; 589.0 nm |
| Slit width | ; 0.2 nm | ; 0.2 nm |
| Lighting mode | ; HCL | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2000 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>589.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0264 |
| 2 | 0.1000 | 0.1553 |
| 3 | 0.3000 | 0.4289 |
| 4 | 0.5000 | 0.6504 |

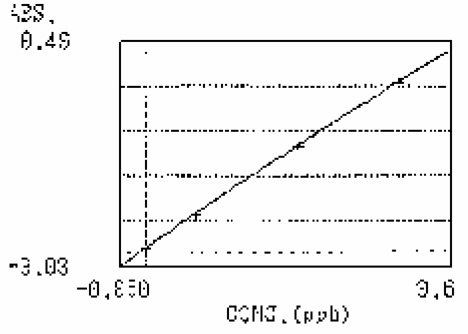


$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9995$

K0= 0.0220, K1= 1.4548, K2= –0.3895

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>589.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0060 |
| 2 | 0.1000 | 0.0686 |
| 3 | 0.3000 | 0.2013 |
| 4 | 0.5000 | 0.3223 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9998$

K0= 0.0047, K1= 0.6702, K2= –0.0682

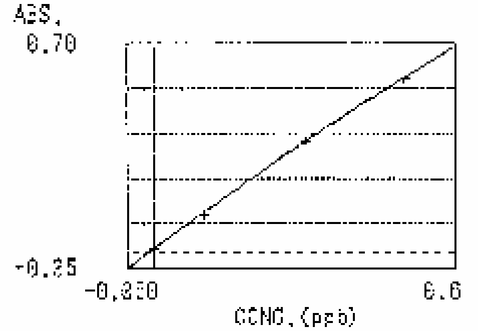
## Sodium (Na)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2000 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>589.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0157 |
| 2 | 0.1000 | 0.1302 |
| 3 | 0.3000 | 0.3730 |
| 4 | 0.5000 | 0.5853 |

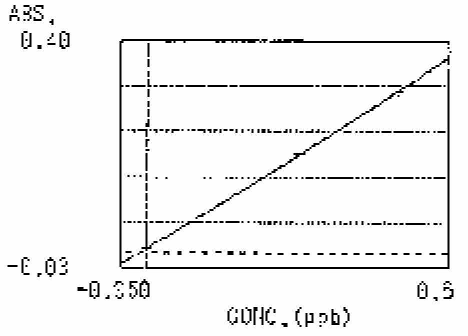


$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9997$

K0= 0.0127, K1= 1.2506, K2= –0.2067

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>589.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0088 |
| 2 | 0.1000 | 0.0575 |
| 3 | 0.3000 | 0.1861 |
| 4 | 0.5000 | 0.3030 |

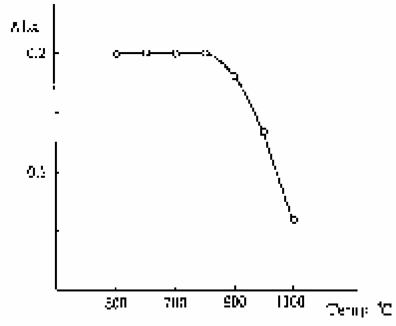


$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9988$

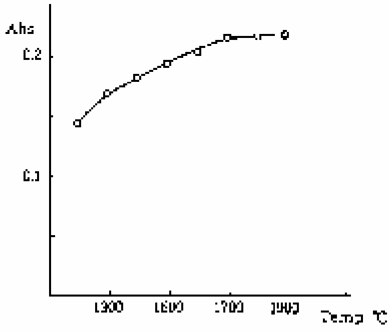
K0= 0.0056, K1= 0.5747, K2= 0.0449

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqueous solution, NaC*l*)

Ashing condition



Atomization condition



## Nickel (Ni)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

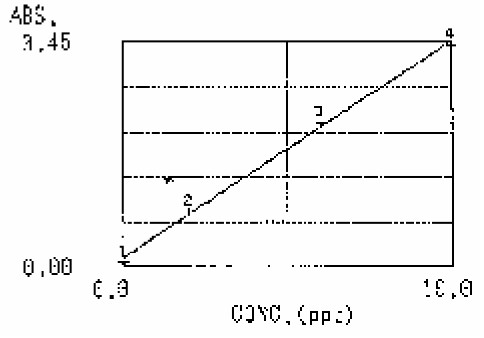
| | | |
|---|---|---|
| Current | ; 12 mA/0 mA | ; 10 mA/400 mA |
| Wavelength | ; 232.0 nm | ; 232.0 nm |
| Slit width | ; 0.2 nm | ; 0.2 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 232.0nm |
| 1 | 0.0000 | 0.0090 |
| 2 | 2.0000 | 0.1083 |
| 3 | 6.0000 | 0.2876 |
| 4 | 10.0000 | 0.4447 |

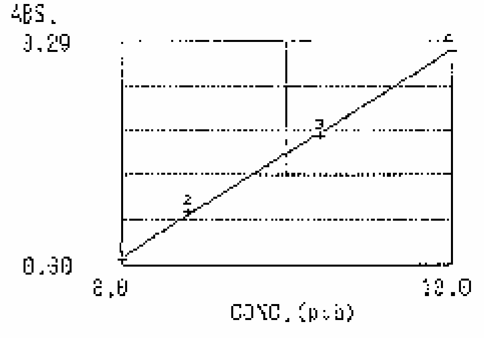


[ABS]=K1*[C]+K0  r2=0.9980

K0= 0.0167, K1= 0.0435

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 232.0nm |
| 1 | 0.0000 | 0.0095 |
| 2 | 2.0000 | 0.0679 |
| 3 | 6.0000 | 0.1680 |
| 4 | 10.0000 | 0.2803 |



[ABS]=K1*[C]+K0  $r^2$=0.9993

K0= 0.0108, K1= 0.0268

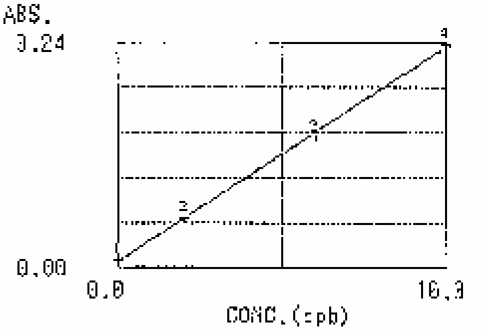
## Nickel (Ni)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 232.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0084 |
| 2 | 2.0000 | 0.0542 |
| 3 | 6.0000 | 0.1397 |
| 4 | 10.0000 | 0.2373 |

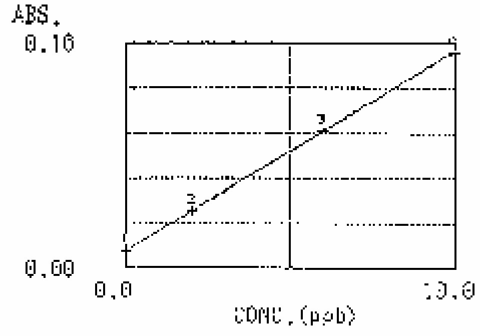


[ABS]=K1*[C]+K0  $r^2$=0.9991

K0= 0.0076, K1= 0.0227

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 232.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0125 |
| 2 | 2.0000 | 0.0411 |
| 3 | 6.0000 | 0.0979 |
| 4 | 10.0000 | 0.1532 |

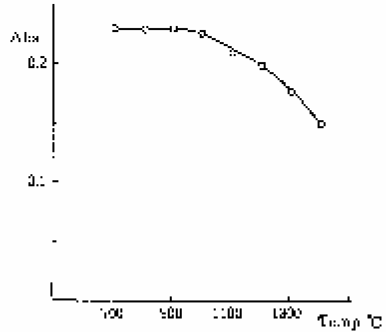


[ABS]=K1*[C]+K0  $r^2$=0.9999

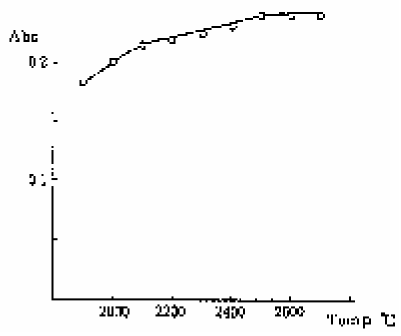
K0= 0.0128, K1= 0.0141

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



## Lead (Pb)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

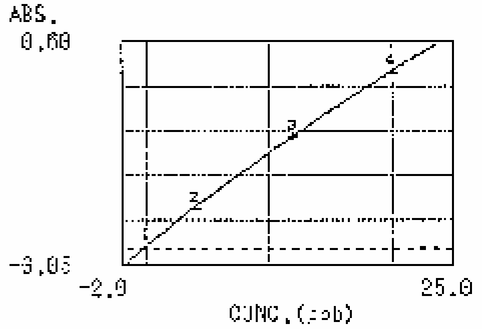
| | | |
|---|---|---|
| Current | ; 10 mA/0 mA | ; 8 mA/300 mA |
| Wavelength | ; 283.3 nm | ; 283.3 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1800 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

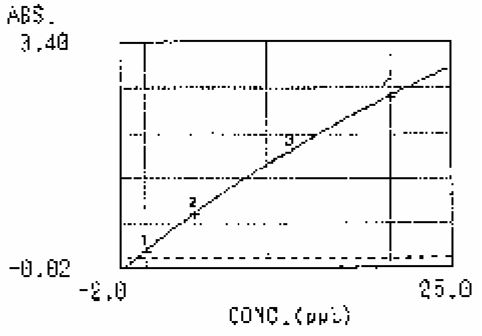
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>283.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0051 |
| 2 | 4.0000 | 0.1128 |
| 3 | 12.0000 | 0.3282 |
| 4 | 20.0000 | 0.5122 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9999
K0= –0.0032, K1= 0.0290, K2= –0.0002

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>283.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0108 |
| 2 | 4.0000 | 0.0823 |
| 3 | 12.0000 | 0.2015 |
| 4 | 20.0000 | 0.3016 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9999
K0= 0.0116, K1= 0.0180, K2= –0.0002

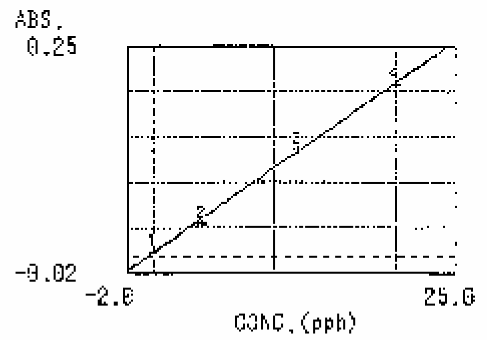
## Lead (Pb)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1800 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 283.3nm |
| 1 | 0.0000 | 0.0063 |
| 2 | 4.0000 | 0.0392 |
| 3 | 12.0000 | 0.1280 |
| 4 | 20.0000 | 0.2044 |

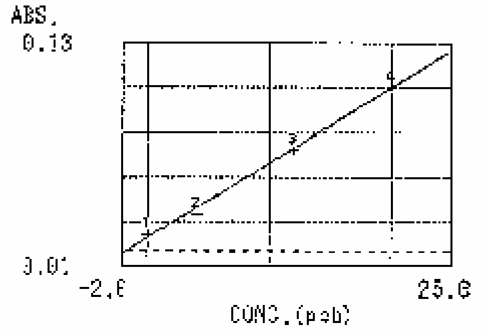


[ABS]=K1*[C]+K0  $r^2=0.9983$

K0= 0.0037, K1= 0.0101

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 283.3nm |
| 1 | 0.0000 | 0.0106 |
| 2 | 4.0000 | 0.0231 |
| 3 | 12.0000 | 0.0637 |
| 4 | 20.0000 | 0.1025 |

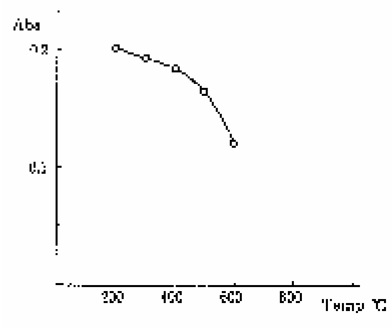


[ABS]=K1*[C]+K0  $r^2=0.9961$

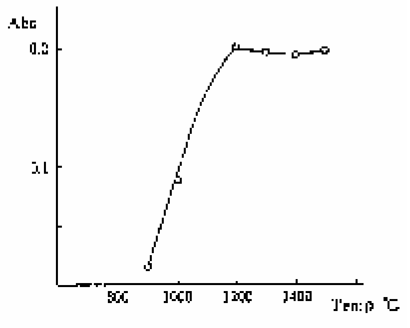
K0= 0.0077, K1= 0.0047

- Ashing temperature, atomization temperature and sensitivity (Solution: $HNO_3$, Metal)

Ashing condition



Atomization condition



# Platinum (Pt)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

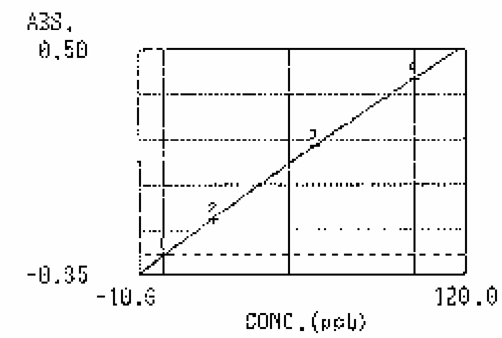
| | |
|---|---|
| Current | ; 14 mA/0 mA |
| Wavelength | ; 266.0 nm |
| Slit width | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>266.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0010 |
| 2 | 20.0000 | 0.0850 |
| 3 | 60.0000 | 0.2662 |
| 4 | 100.0000 | 0.4285 |



$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9997$

K0= –0.0012, K1= 0.0046, K2= –0.0000

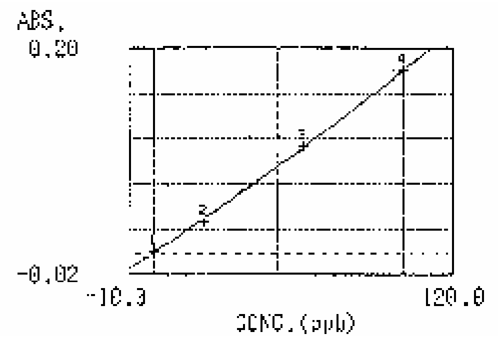
## Platinum (Pt)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 266.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0027 |
| 2 | 20.0000 | 0.0313 |
| 3 | 60.0000 | 0.1039 |
| 4 | 100.0000 | 0.1768 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9995

K0= 0.0015, K1= 0.0016, K2= 0.0000

# Rhodium (Rh)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

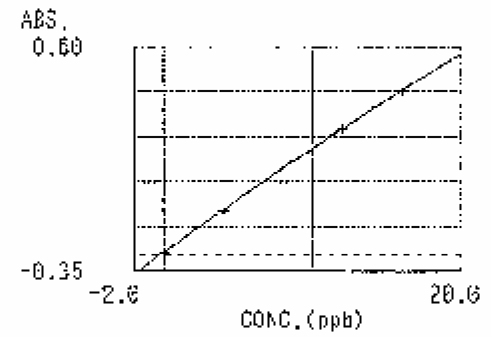
| | |
|---|---|
| Current | ; 12 mA/0 mA |
| Wavelength | ; 343.5 nm |
| Slit width | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

| STD. No. | CONC. (ppb) | ABS. 343.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0051 |
| 2 | 4.0000 | 0.1284 |
| 3 | 12.0000 | 0.3635 |
| 4 | 16.0000 | 0.4732 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=1.0000

K0= 0.0049, K1= 0.0315, K2= –0.0001

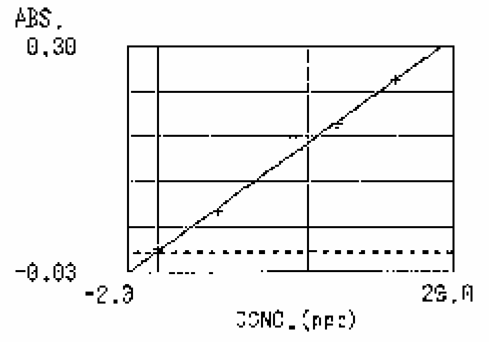
## Rhodium (Rh)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>343.5nm |
|---|---|---|
| 1 | 0.0000 | 0.0043 |
| 2 | 4.0000 | 0.0585 |
| 3 | 12.0000 | 0.1875 |
| 4 | 16.0000 | 0.2519 |



[ABS]=K1*[C]+K0  $r^2$=0.9991

K0= 0.0007, K1= 0.0156

# Antimony (Sb)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

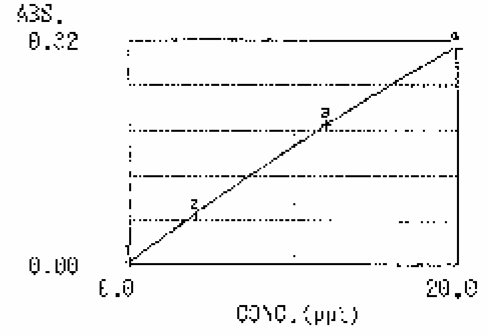
| | | |
|---|---|---|
| Current | ; 13 mA/0 mA | ; 15 mA/500 mA |
| Wavelength | ; 217.6 nm | ; 217.6 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube Pd 10 ppm added

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

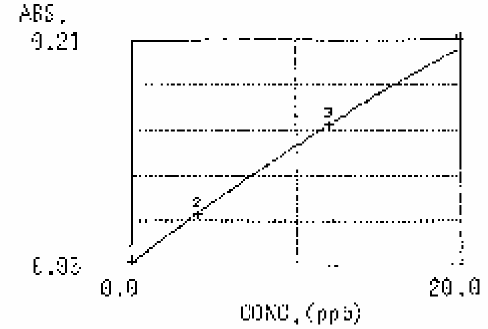
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>217.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0043 |
| 2 | 4.0000 | 0.0722 |
| 3 | 12.0000 | 0.2011 |
| 4 | 20.0000 | 0.3111 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=1.0000
K0= 0.0037, K1= 0.0179, K2= –0.0001

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>217.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0036 |
| 2 | 4.0000 | 0.0481 |
| 3 | 12.0000 | 0.1325 |
| 4 | 20.0000 | 0.2010 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=0.9999
K0= 0.0031, K1= 0.0019, K2= –0.0001

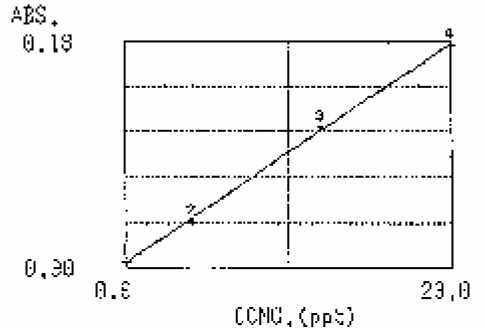
## Antimony (Sb)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube Pd 10 ppm added

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

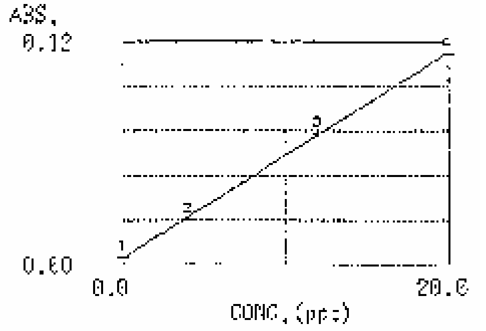
| STD. No. | CONC. (ppb) | ABS. 217.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0055 |
| 2 | 4.0000 | 0.0377 |
| 3 | 12.0000 | 0.1113 |
| 4 | 20.0000 | 0.1775 |



[ABS]=K1*[C]+K0 $r^2$=0.9994
K0= 0.0049, K1= 0.0087

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

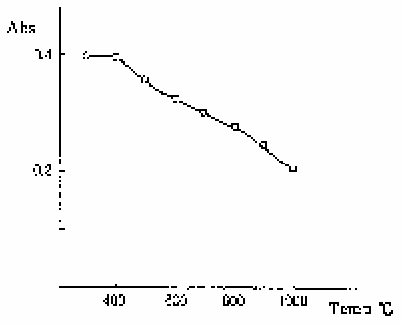
| STD. No. | CONC. (ppb) | ABS. 217.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0043 |
| 2 | 4.0000 | 0.0249 |
| 3 | 12.0000 | 0.0711 |
| 4 | 20.0000 | 0.1133 |



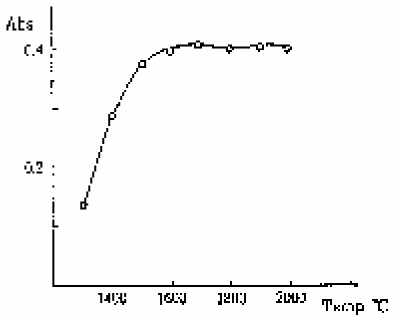
[ABS]=K1*[C]+K0 $r^2$=0.9996
K0= 0.0040, K1= 0.0055

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



## Selenium (Se)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

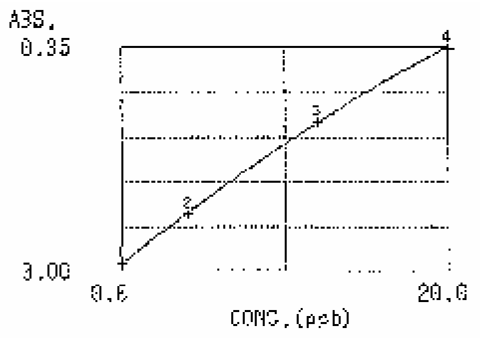
Current ; 23 mA/0 mA
Wavelength ; 196.0 nm
Slit width ; 0.5 nm
Lighting mode ; BGC-$D_2$

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube Pd 10 ppm added

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 µ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>196.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0130 |
| 2 | 4.0000 | 0.0900 |
| 3 | 12.0000 | 0.2336 |
| 4 | 20.0000 | 0.3491 |



[ABS]=K2*[C]2+K1*[C]+K0 $r^2$=0.9999
K0= 0.0121, K1= 0.0206, K2= –0.0002

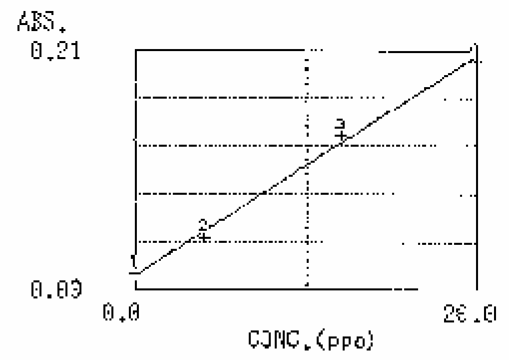
## Selenium (Se)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube Pd 10 ppm added

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 600 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 600 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2200 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

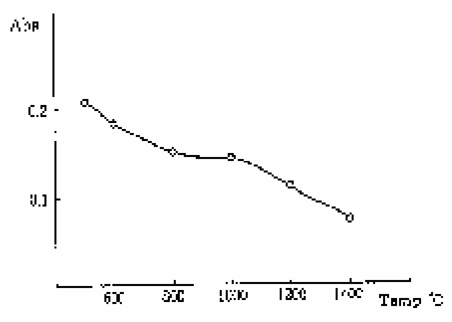
| STD. No. | CONC. (ppb) | ABS. 196.0nm |
|---|---|---|
| 1 | 0.0000 | 0.0142 |
| 2 | 4.0000 | 0.0466 |
| 3 | 12.0000 | 0.1347 |
| 4 | 20.0000 | 0.2023 |



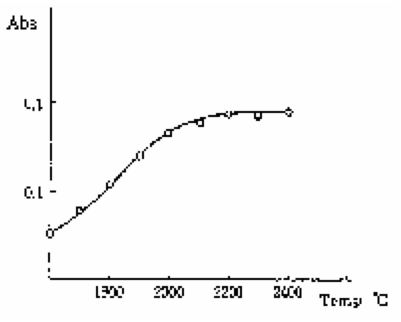
[ABS]=K1*[C]+K0  $r^2$=0.9966
K0= 0.0130, K1= 0.0096

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



## Silicon (Si)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

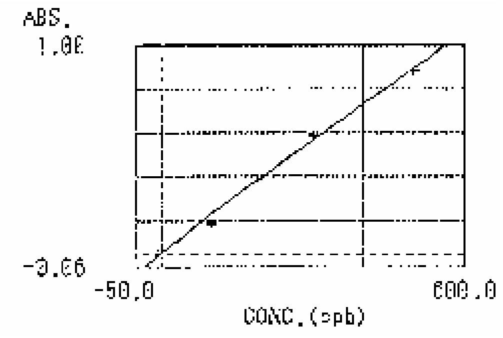
| | | |
|---|---|---|
| Current | ; 15 mA/0 mA | ; 10 mA/500 mA |
| Wavelength | ; 251.6 nm | ; 251.6 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

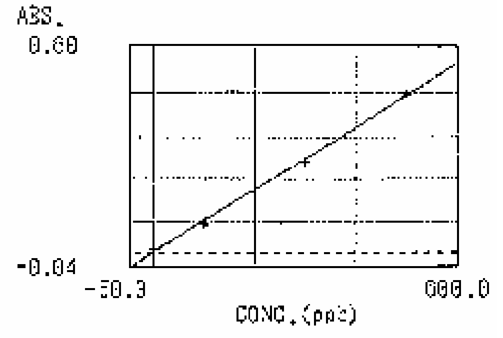
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>251.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0257 |
| 2 | 100.0000 | 0.1458 |
| 3 | 300.0000 | 0.5657 |
| 4 | 500.0000 | 0.8814 |



[ABS]=K2*[C]2+K1*[C]+K0  $r^2$=0.9942
K0= 0.0050, K1= 0.0018, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>251.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0123 |
| 2 | 100.0000 | 0.0841 |
| 3 | 300.0000 | 0.2708 |
| 4 | 500.0000 | 0.4654 |



[ABS]=K1*[C]+K0  $r^2$=0.9979
K0= 0.0022, K1= 0.0009

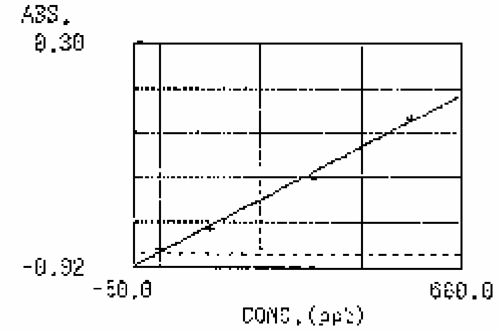
## Silicon (Si)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

| STD. No. | CONC. (ppb) | ABS. 251.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0069 |
| 2 | 100.0000 | 0.0353 |
| 3 | 300.0000 | 0.1077 |
| 4 | 500.0000 | 0.1922 |

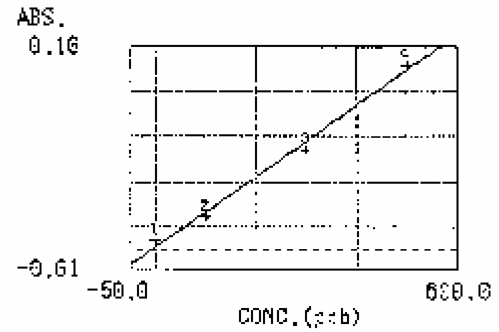


[ABS]=K1*[C]+K0  $r^2$=0.9956

K0= 0.0017, K1= 0.0004

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD. No. | CONC. (ppb) | ABS. 251.60nm |
|---|---|---|
| 1 | 0.0000 | 0.0047 |
| 2 | 100.0000 | 0.0166 |
| 3 | 300.0000 | 0.0494 |
| 4 | 500.0000 | 0.0914 |

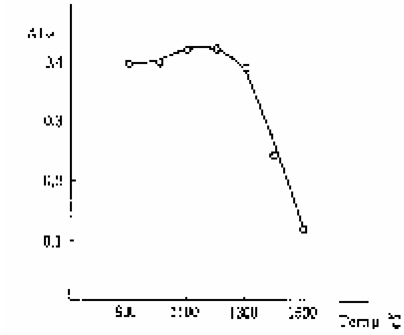


[ABS]=K1*[C]+K0  $r^2$=0.9906

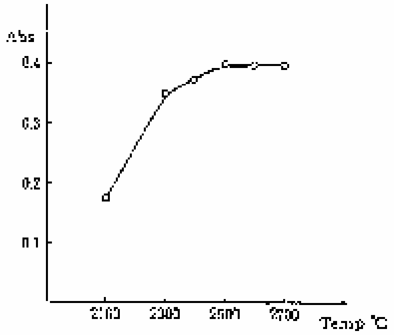
K0= 0.0013, K1= 0.0002

- Ashing temperature, atomization temperature and sensitivity (Solution: $Na_2CO_3$, $Na_2SiO_2$)

Ashing condition



Atomization condition



## Tin (Sn) I

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

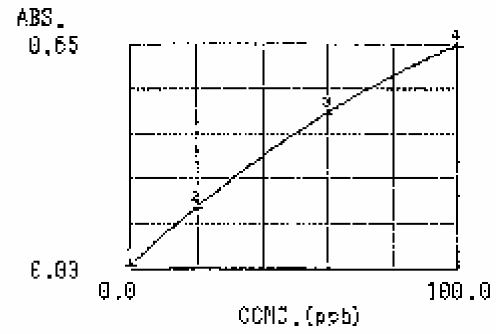
Current ; 14 mA/0 mA
Wavelength ; 224.6 nm
Slit width ; 1.0 nm
Lighting mode ; BGC-$D_2$

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube Pd 10 ppm added

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>224.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0117 |
| 2 | 20.0000 | 0.1768 |
| 3 | 60.0000 | 0.4504 |
| 4 | 100.0000 | 0.6448 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=1.0000
K0= 0.0115, K1= 0.0088, K2= –0.0000

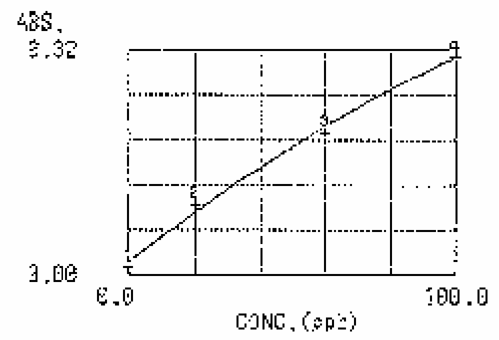
## Tin (Sn) I

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube, Pd 10 ppm added

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 224.6nm |
|---|---|---|
| 1 | 0.0000 | 0.0113 |
| 2 | 20.0000 | 0.1019 |
| 3 | 60.0000 | 0.2031 |
| 4 | 100.0000 | 0.3103 |



$[ABS]=K2*[C]^2+K1*[C]+K$  $r^2=0.9943$

K0= 0.0181, K1= 0.0037, K2= –0.0000

# Tin (Sn) II

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

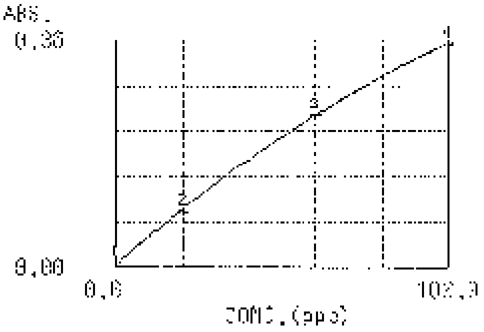
| | | |
|---|---|---|
| Current | ; | 10 mA/0 mA |
| Wavelength | ; | 286.3 nm |
| Slit width | ; | 1.0 nm |
| Lighting mode | ; | BGC-$D_2$ |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube, Pd 10 ppm added

| STAGE# | TEMP.($^{o}$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 286.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0066 |
| 2 | 20.0000 | 0.0899 |
| 3 | 60.0000 | 0.2437 |
| 4 | 100.0000 | 0.3555 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9998
K0= 0.0051, K1= 0.0046, K2= –0.0000

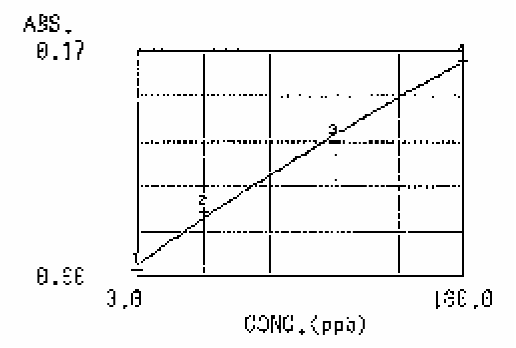
## Tin (Sn) II

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube, Pd 10 ppm added

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 800 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 800 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2400 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 286.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0055 |
| 2 | 20.0000 | 0.0498 |
| 3 | 60.0000 | 0.1029 |
| 4 | 100.0000 | 0.1617 |

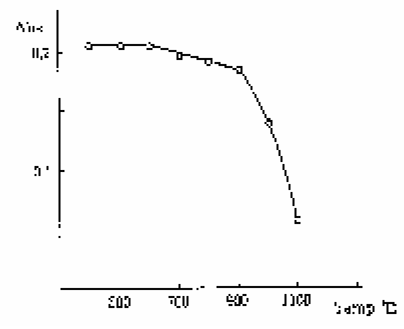


$[ABS]=K2*[C]^2+K1*[C]+K0 \quad r^2=0.9953$

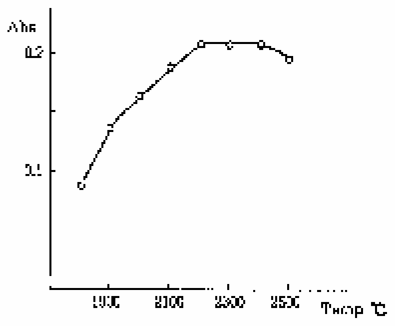
K0= 0.0087, K1= 0.0018, K2= –0.0000

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, Metal)

Ashing condition



Atomization condition



## Strontium (Sr)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

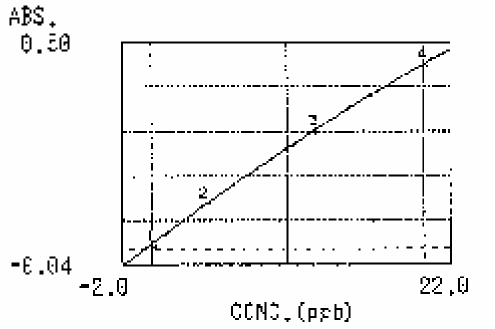
Current ; 8 mA/0 mA
Wavelength ; 460.7 nm
Slit width ; 0.5 nm
Lighting mode ; HCL

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 460.7nm |
| 1 | 0.0000 | 0.0072 |
| 2 | 4.0000 | 0.1074 |
| 3 | 12.0000 | 0.2852 |
| 4 | 20.0000 | 0.4452 |



[ABS]=K2*[C]$^2$+K1*[C]+K0 $r^2$=1.0000
K0= 0.0080, K1= 0.0252, K2= –0.0002

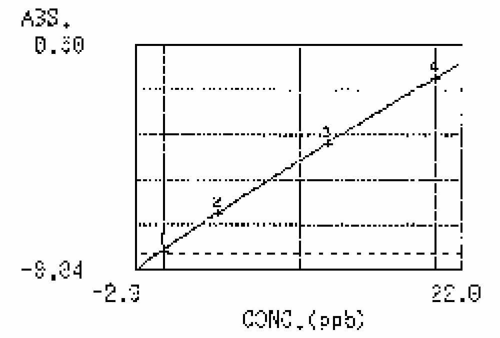
## Strontium (Sr)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 500 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 500 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2300 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in HCL mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 460.7nm |
|---|---|---|
| 1 | 0.0000 | 0.0077 |
| 2 | 4.0000 | 0.0958 |
| 3 | 12.0000 | 0.2646 |
| 4 | 20.0000 | 0.4206 |

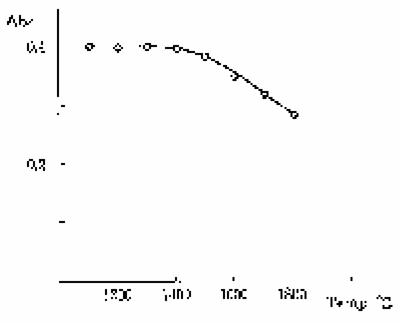


$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=1.0000$

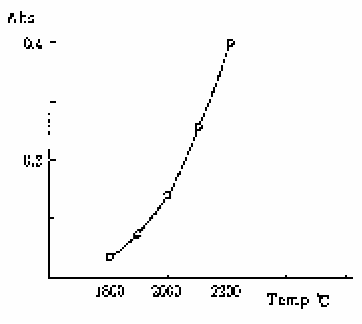
K0= 0.0075, K1= 0.0225, K2= –0.0000

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, $SrCO_3$)

Ashing condition



Atomization condition



## Titanium (Ti)

### Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

### Measuring conditions and calibration curve

- Lighting conditions

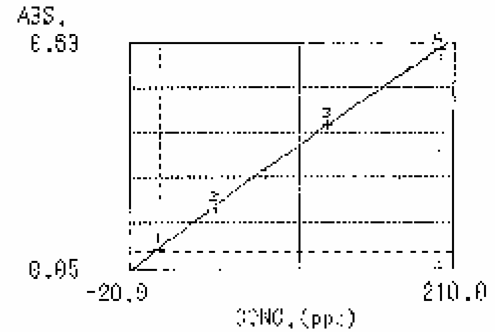
Current ; 12 mA/0 mA ; 10 mA/600 mA
Wavelength ; 364.3 nm ; 364.3 nm
Slit width ; 0.5 nm ; 0.5 nm
Lighting mode ; BGC-$D_2$ ; BGC-SR

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 $\mu l$)

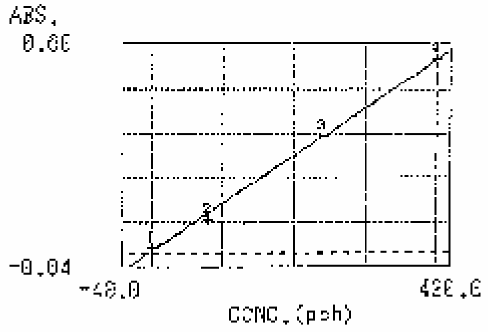
| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 364.3nm |
| 1 | 0.0000 | 0.0074 |
| 2 | 40.0000 | 0.1208 |
| 3 | 120.0000 | 0.3642 |
| 4 | 200.0000 | 0.5803 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9997
K0= 0.0044, K1= 0.0031, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 $\mu l$)

| STD. | CONC. | ABS. |
|---|---|---|
| No. | (ppb) | 364.3nm |
| 1 | 0.0000 | 0.0147 |
| 2 | 80.0000 | 0.0978 |
| 3 | 240.0000 | 0.3351 |
| 4 | 400.0000 | 0.5543 |



[ABS]=K1*[C]+K0  $r^2$=0.9979
K0= 0.0033, K1= 0.0014

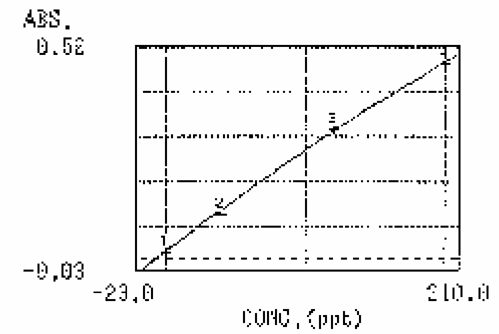
## Titanium (Ti)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2600 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 364.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0166 |
| 2 | 40.0000 | 0.1079 |
| 3 | 120.0000 | 0.3034 |
| 4 | 200.0000 | 0.4607 |

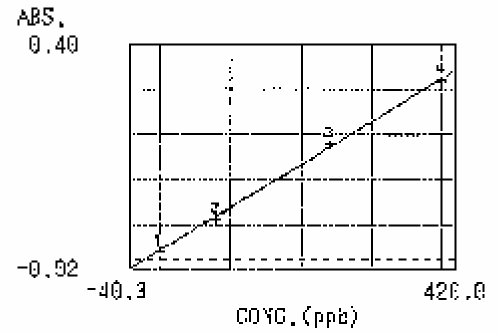


$[ABS]=K2*[C]^2+K1*[C]+K0$  $r^2=0.9994$

K0= 0.0133, K1= 0.0026, K2= –0.0000

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 364.3nm |
|---|---|---|
| 1 | 0.0000 | 0.0127 |
| 2 | 80.0000 | 0.0756 |
| 3 | 240.0000 | 0.2151 |
| 4 | 400.0000 | 0.3325 |

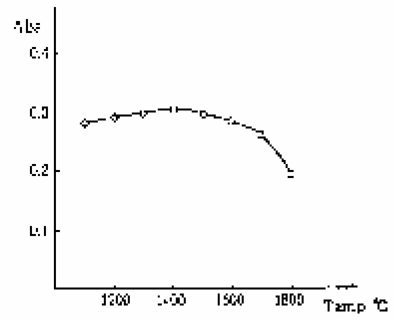


$[ABS]=K1*[C]+K0$  $r^2=0.9986$

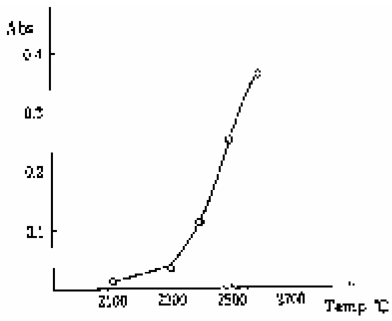
K0= 0.0137, K1= 0.0008

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, Metal)

Ashing condition



Atomization condition



# Vanadium (V)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

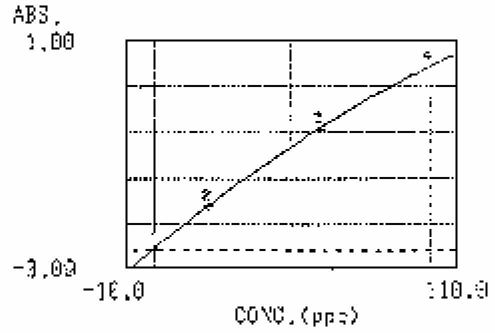
Current ; 10 mA/0 mA
Wavelength ; 318.4 nm
Slit width ; 0.5 nm
Lighting mode ; BGC-$D_2$

- Graphite furnace temperature program (High sensitivity mode 0. 0H), Pyrolytic graphite tube

| STAGE# | TEMP.($^oC$) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 900 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 900 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>318.4nm |
|---|---|---|
| 1 | 0.0000 | 0.0048 |
| 2 | 20.0000 | 0.2104 |
| 3 | 60.0000 | 0.5760 |
| 4 | 100.0000 | 0.8696 |



[ABS]=K2*$[C]^2$+K1*[C]+K0 $r^2$=1.0000
K0= 0.0041, K1= 0.0108, K2= –0.0000

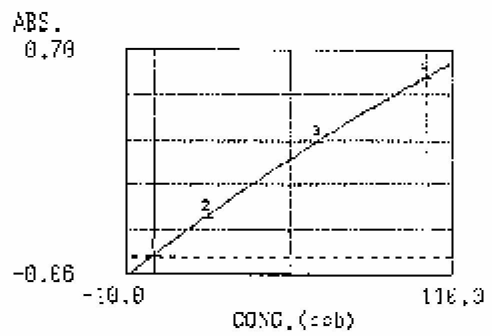
## Vanadium (V)

- Graphite furnace temperature program (Standard mode 0. 0), Pyrolytic graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 700 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 700 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 2700 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 318.4nm |
|---|---|---|
| 1 | 0.0000 | 0.0064 |
| 2 | 20.0000 | 0.1360 |
| 3 | 60.0000 | 0.3915 |
| 4 | 100.0000 | 0.6061 |

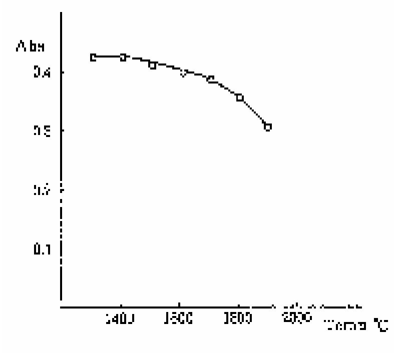


[ABS]=K2*$[C]^2$+K1*[C]+K0  $r^2$=0.9999

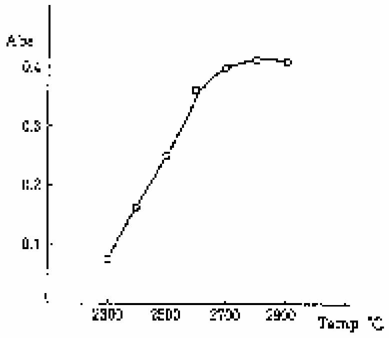
K0= 0.0042, K1= 0.0070, K2= –0.0000

- Ashing temperature, atomization temperature and sensitivity (Solution: Aqua Regia, Metal)

Ashing condition



Atomization condition



# Zinc (Zn)

## Standard substance and standard solution preparation method

Refer to Section 3 - 3 for the standard solution preparation method

## Measuring conditions and calibration curve

- Lighting conditions

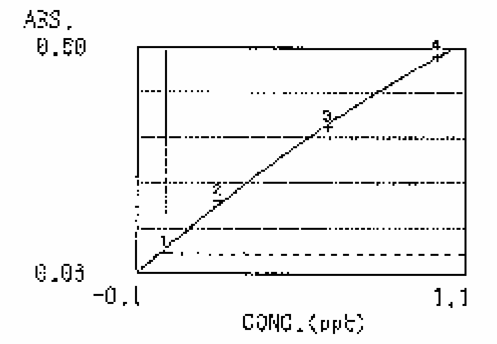
| | | |
|---|---|---|
| Current | ; 8 mA/0 mA | ; 10 mA/300 mA |
| Wavelength | ; 213.9 nm | ; 213.9 nm |
| Slit width | ; 0.5 nm | ; 0.5 nm |
| Lighting mode | ; BGC-$D_2$ | ; BGC-SR |

- Graphite furnace temperature program (High sensitivity mode 0. 0H), High density graphite tube

| STAGE# | TEMP.($^o$C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0H | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0H | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

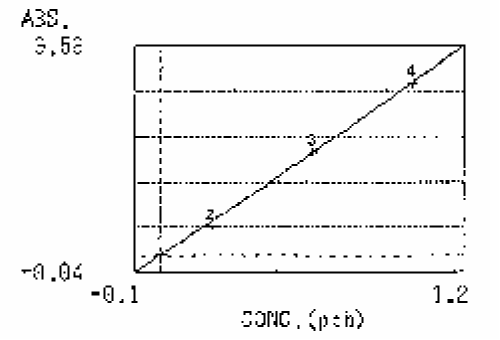
| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>213.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0053 |
| 2 | 0.2000 | 0.1509 |
| 3 | 0.6000 | 0.3676 |
| 4 | 1.0000 | 0.5764 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9990
K0= 0.0108, K1= 0.6700, K2= –0.1065

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD.<br>No. | CONC.<br>(ppb) | ABS.<br>213.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0053 |
| 2 | 0.2000 | 0.0808 |
| 3 | 0.6000 | 0.2399 |
| 4 | 1.0000 | 0.3635 |



[ABS]=K2*[C]$^2$+K1*[C]+K0  r$^2$=0.9994
K0= 0.0025, K1= 0.4313, K2= –0.0693

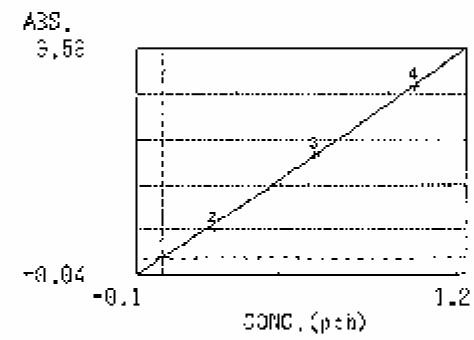
## Zinc (Zn)

- Graphite furnace temperature program (Standard mode 0. 0), High-density graphite tube

| STAGE# | TEMP.(°C) | TIME (sec) | GAS | (l/min) | HEAT | SAMPLING | PreTIME |
|---|---|---|---|---|---|---|---|
| 1 | 120 | 20 | #1 | 1.0 | RAMP | OFF | |
| 2 | 250 | 10 | #1 | 1.0 | RAMP | OFF | |
| 3 | 300 | 10 | #1 | 1.0 | STEP | OFF | |
| 4 | 300 | 3 | #1 | 0.0 | STEP | OFF | |
| 5 | 1500 | 3 | #1 | 0.0 | STEP | ON | 2 |

- Calibration curve in BGC-$D_2$ mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 213.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0034 |
| 2 | 0.2000 | 0.0727 |
| 3 | 0.6000 | 0.2483 |
| 4 | 1.0000 | 0.4113 |

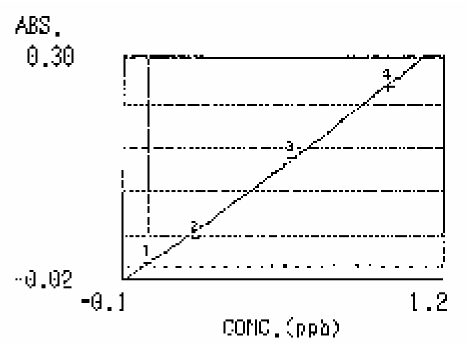


[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9991

K0=-0.0004, K1= 0.3971, K2= 0.0160

- Calibration curve in BGC-SR mode (Sample injection volume 20 μ*l*)

| STD. No. | CONC. (ppb) | ABS. 213.9nm |
|---|---|---|
| 1 | 0.0000 | 0.0060 |
| 2 | 0.2000 | 0.0409 |
| 3 | 0.6000 | 0.1573 |
| 4 | 1.0000 | 0.2622 |

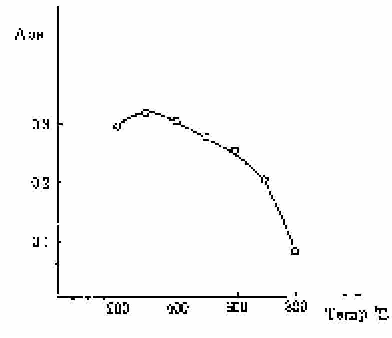


[ABS]=K2*[C]$^2$+K1*[C]+K0  $r^2$=0.9970

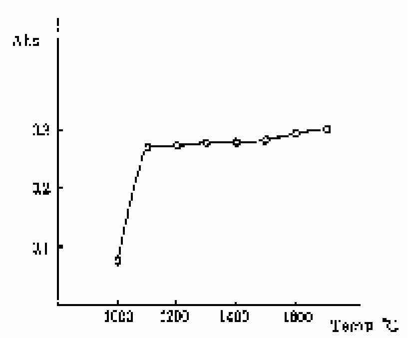
K0= 0.0016, K1= 0.2323, K2= 0.0300

- Ashing temperature, atomization temperature and sensitivity (Solution: HC*l*, Metal)

Ashing condition



Atomization condition



# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 5

### Water Analysis and Air Analysis

SHIMADZU CORPORATION

## Atomic Absorption Spectrophotometer Cookbook

## Section 5

# CONTENTS

# 8. Water Analysis

## 8.1 Analysis of city water

**Reference** : City water testing method 1993 edition by Japan Waterworks Association

### 8.1.1 Preservation of sample

Nitric acid is added to the sample water at the rate of 10 m*l* per one liter. Hydrochloric acid is added instead of nitric acid to measure As, Se or Sb by the hydride vapor generation method.

### 8.1.2 Furnace analysis method

**a) Target elements**

A1, As, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Pb, Sb, Se and Zn

**b) Pretreatment of samples**

◦ Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se and Zn

100 m*l* of sampled water (containing nitric acid at the rate 1 m*l* per 100 m*l*) is taken in a 200 m*l* flask, heated avoiding boiling to about 8 m*l*. After cooling, it is put together with flask wash liquid and is increased to 10 m*l* with water. 1/10 concentrated liquid is prepared and used for measurement. If the target element concentration in the 1/10 concentrated sample solution is higher than the concentration range of the calibration curve described later, the sampling amount is made smaller than 100 m*l* to lower the concentration rate or the sampled water is measured directly.

◦ Na

The sampled water (containing nitric acid at the rate of 1 m*l* per 100 m*l*) is directly measured or diluted to the concentration range of the calibration curve to be used for measurement. If it is muddy, it must be removed in advance by filtering.

**c) Measuring operation**

Reagent standard solution

Refer to the cookbook section 2, paragraph 3, and standard reagent preparation of the standard solution for calibration curve of each element.

**Operation**

The pretreated sample is used for measurement as it is. If the influence of interfering substances is expected, the method using matrix modifiers is used. In this method, about 100 μ*l* of the sample is taken and the matrix modifier (concentration of about 10 μg/m*l*) of the same volume is added and mixed well as the measuring sample. If the influence of interfering substances cannot be removed even by using the method of matrix modifiers, the standard addition method is used for measurement.

Interfering substances and matrix modifiers are shown in the measuring conditions of this publication. Also, refer to the cookbook section 2, paragraph 5.3 and section 4, paragraph 7.4.

**Measurement**

Measurement is made under the following conditions for each element. Refer to the cookbook section 4, paragraph 7.4, “Measuring conditions for lamp current value and slit width of the atomic absorption spectrophotometer”.

◦ **Al**

| | |
|---|---|
| Measuring wavelength | 309.3 nm |
| Calibration curve concentration range | 2 to 20 ng/m*l* |
| Tube | Pyrolytic graphite tube |
| Sample injection amount | 20 μ*l* |
| Heating condition | |

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 7 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2400 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Positive interference with Mg 50 mg/*l* and negative interference with Ca 100 mg/*l* or Fe 50 mg/*l*.

Magnesium nitrate or ammonium chloride is added.

◦ **As**

| | |
|---|---|
| Measuring wavelength | 193.7 nm |
| Calibration curve concentration range | 1 to 20 ng/m*l* |
| Tube | High-density graphite tube (Pd 10 ppm added) |
| Sample injection amount | 20 μ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 7 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Negative interference with Ca 500 mg/*l*, Na 500 mg/*l* or Fe 50 mg/*l*. Palladium (II) nitrate or nickel nitrate is added.

- **Cd**

| | |
|---|---|
| Measuring wavelength | 228.8 nm |
| Calibration curve concentration range | 0.1 to 1 ng/m*l* |
| Tube | High-density graphite tube (Pd 10 ppm added) |
| Sample injection amount | 10 µ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 7 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Matrix modifiers

Palladium (II) nitrate and ammonium nitrate

- **Cr**

| | |
|---|---|
| Measuring wavelength | 357.9 nm |
| Calibration curve concentration range | 1 to 5 ng/m*l* |
| Tube | Pyrolytic graphite tube |
| Sample injection amount | 10 µ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 7 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2400 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Positive interference with Mg 50 mg/*l* and negative interference with Ca 500 mg/*l*, ammonium chloride is added.

Remarks : When only Cr (VI) is analyzed, remove the coexistent Cr (III) by the following Fe co precipitation method.

100 m*l* of the sample is taken and 1 m*l* of ammonium iron (III) sulfate solution [5g of $(NH_4)$ Fe $(SO_4)_2$ $(12H_2O)$ is dissolved in 1 m*l* of sulfuric acid (1+1) and increased to 100 m*l* with water] is added and mixed. Then, ammonia water (1+1) is added to be slightly alkaline and it is gently heated until the ammonia smell almost disappears. After letting it stand for about 15 minutes, filter and washes it, with ammonium nitrate solution (1 w/v%), and heat it, at about 50 °C. 2 m*l* of nitric acid is added and the total volume is increased to 300 m*l* with water by putting filter and wash liquid together. This is used for measurement.

◦ **Cu**

| | |
|---|---|
| Measuring wavelength | 324.8 nm |
| Calibration curve concentration range | 10 to 50 ng/m*l* |
| Tube | High-density graphite tube |
| Sample injection amount | 20 µ*l* |
| Heating condition | |

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 7 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2500 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- **Fe**

| | |
|---|---|
| Measuring wavelength | 248.3 nm |
| Calibration curve concentration range | 20 to 100 ng/m*l* |
| Tube | High-density graphite tube |
| Sample injection amount | 20 μ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 7 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2500 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- **Mn**

| | |
|---|---|
| Measuring wavelength | 279.5 nm |
| Calibration curve concentration range | 2 to 10 ng/m*l* |
| Tube | High-density graphite tube |
| Sample injection amount | 20 μ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 800 | 10 | R | 1.0 |
| 4 | 800 | 7 | S | 1.0 |
| 5 | 800 | 3 | S | 0.0H |
| 6 | 2500 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

Matrix modifiers

Magnesium nitrate and ammonium chloride.

- **Mo**

| | |
|---|---|
| Measuring wavelength | 313.3 nm |
| Calibration curve concentration range | 10 to 50 ng/m*l* |
| Tube | Pyrolytic graphite tube |
| Sample injection amount | 20 μ*l* |

|  | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 900 | 10 | R | 1.0 |
| 4 | 900 | 7 | S | 1.0 |
| 5 | 900 | 3 | S | 0.0H |
| 6 | 2700 | 3 | S | 0.0H |
| 7 | 2800 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Positive interference with Ca 500 mg/*l* and ascorbic acid is added.

- **Na**

|  |  |
|---|---|
| Measuring wavelength | 589.0 nm |
| Calibration curve concentration range | 5 to 20 ng/m*l* |
| Tube | High-density graphite tube |
| Sample injection amount | 10 μ*l* |
| Heating condition |  |

|  | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 450 | 10 | R | 1.0 |
| 4 | 450 | 7 | S | 1.0 |
| 5 | 450 | 3 | S | 0.0 |
| 6 | 1800 | 3 | S | 0.0 |
| 7 | 2400 | 2 | S | 1.0 |

- **Ni**

|  |  |
|---|---|
| Measuring wavelength | 232.0 nm |
| Calibration curve concentration range | 2 to 20 ng/m*l* |
| Tube | Pyrolytic graphite tube |
| Sample injection amount | 20 μ*l* |
| Heating condition |  |

|  | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 800 | 10 | R | 1.0 |
| 4 | 800 | 7 | S | 1.0 |
| 5 | 800 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Positive interference with Fe 50 mg/*l* and magnesium nitrate or ammonium chloride is added.

- **Pb**

| | |
|---|---|
| Measuring wavelength | 283.3 nm |
| Calibration curve concentration range | 1 to 20 ng/m*l* |
| Tube | High-density graphite tube (Pd 10 ppm added) |
| Sample injection amount | 20 μ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 7 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Positive interference with Mg 100 mg/*l*, Ca 500 mg/*l* or Na 500 mg/*l*. Palladium (II) nitrate or ammonium chloride is added.

- **Sb**

| | |
|---|---|
| Measuring wavelength | 217.6 nm |
| Calibration curve concentration range | 2 to 20 ng/m*l* |
| Tube | Pyrolytic graphite tube (Pd 10 ppm added) |
| Sample injection amount | 20 μ*l* |

Heating condition

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 7 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2200 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

Interfering substances and matrix modifiers

Negative interference with Mg 50 mg/*l*, Ca 500 mg/*l* or Ge 5 mg/*l*. Palladium (II) nitrate or nickel nitrate is added.

- **Se**

| | |
|---|---|
| Measuring wavelength | 196.0 nm |
| Calibration curve concentration range | 2 to 30 ng/m*l* |
| Tube | High-density graphite tube (Pd 10 ppm added) |
| Sample injection amount | 20 μ*l* |
| Heating condition | |

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 7 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Zn**

| | |
|---|---|
| Measuring wavelength | 213.9 nm |
| Calibration curve concentration range | 1 to 4 ng/m*l* |
| Tube | High-density graphite tube |
| Sample injection amount | 10 m*l* |
| Heating condition | |

| | TEMP(°C) | TIME(sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 10 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 450 | 10 | R | 1.0 |
| 4 | 450 | 7 | S | 1.0 |
| 5 | 450 | 3 | S | 0.0 |
| 6 | 1800 | 3 | S | 0.0 |
| 7 | 2400 | 2 | S | 1.0 |

### 8.1.3 Hydride vapor generation analysis method

**a) Target elements**

As, Sb and Se

**b) Pretreatment of sample**

- **As**

  To the 100 m*l* sample taken, 4 m*l* of hydrochloric acid (1+1) and 2 m*l* of potassium iodide solution (200 g/*l*) are added. In addition, heat it without boiling.

  After letting it cool, increase it up to 20 m*l* with water and use it for measurement.

- **Sb and Se**

  4 m*l* of hydrochloric acid (1+1) is added to 100 m*l* of the sampled water and heat it avoiding boiling. After it has cooled, increase to 20 m*l* and use for measurement.

**c) Measuring operation**

- **As**

**Reagent**

(1) As standard solution (1 μg As/m*l*) :
Refer to the cookbook section 2, paragraph 3 standard sample preparation.

(2) Sodium tetrahydroborate solution (0.5 w/v%) :
2.5 g of sodium tetrahydroborate is dissolved in 500 m*l* of sodium hydroxide solution (0.1 mol/*l*).

(3) Hydrochloric acid

**Operation**

(1) The pretreated sample is used for measurement as it is.

(2) For the calibration curve, 10 to 40 ng of As are taken from the As standard solution (1 μg As/m*l*) into some flasks. 4 m*l* of hydrochloric acid (1+1) and 2 m*l* of potassium iodide solution (200 g/*l*) are added to each flask. Then, they are heated, without boiling. Increase to 20 m*l* with water after it has cooled and use it for measurement.

**Measurement**

The hydride vapor generator (HVG-1) is connected to the atomic absorption spectrophotometer to measure the sample.

Refer to the HVG-1 operation manual for its operation.

Measuring wavelength 193.7 nm

| | | |
|---|---|---|
| Calibration curve concentration range | 0.5 to 2 ng/m*l* | |
| Measuring condition | Lamp current value | 14 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |

- **Sb**

**Reagent**

(1) Sb standard solution (1 μg Sb/m*l*) :

Refer to the cookbook section 2, paragraph 3, standard sample preparation method.

(2) Sodium tetrahydroborate solution (0.5 w/v%) :

Same as As reagent (2) above.

(3) Hydrochloric acid

**Operation**

(1) The pretreated sample is used for measurement as it is.

(2) For the calibration curve, 20 to 100 m*l* of Sb is taken from the Sb standard (1 μg Sb/m*l*) by stages, and 4 m*l* of hydrochloric acid (1+1) is added.

Increase it up to 20 m*l* with water and used for measurement.

**Measurement**

Measurement is made in the same way as As.

| | | |
|---|---|---|
| Measuring wavelength | 217.6 nm | |
| Calibration curve concentration range | 1 to 5 ng/m*l* | |
| Measuring condition | Lamp current value | 13 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |

- **Se**

**Reagent**

(1) Se standard solution (1 μg Se/m*l*) :

Refer to the cookbook section 2, paragraph 3, standard sample preparation method.

(2) Sodium tetrahydroborate (0.5 w/v%) : Same as As reagent (2) above.

(3) Hydrochloric acid

**Operation**

(1) The pretreated sample is used for measurement as it is.

(2) For the calibration curve, 20 to 100 ng of Se from the Se standard (1 µg Se/m*l*) are taken by stages, and 4 m*l* of hydrochloric acid (1+1) is added. Increase it up to 20 m*l* with water and use it for measurement.

**Measurement**

Measurement is made in the same way as As.

| | | |
|---|---|---|
| Measuring wavelength | 196.0 nm | |
| Calibration curve concentration range | 1 to 5 ng/m*l* | |
| Measuring condition | Lamp current value | 23 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |

### 8.1.4 Mercury reduction vapor atomization method

**a) Target element**

Total Hg

**b) Pretreatment of sample**

200 m*l* of the sample is taken in a flask with a reflux condenser. 20 m*l* of sulfuric acid (1+1), 5 m*l* of nitric acid and 20 m*l* of potassium permanganate solution (5 w/v%) are added. It is heated at 95 °C for two hours. After let it cooled, hydrochloric acid hydroxylamine (10 w/v%) is added, to reduce surplus potassium permanganate. Then increased to 250 m*l* with water for measurement.

When the pollution by organic substances is low, 20 m*l* of sulfuric acid (1+1) is added to the sample and increased to 250 m*l* with water. It may be used for measurement.

**c) Measuring operation**

**Reagent**

(1) Hg standard solution (0.1 µg Hg/m*l*) :
Refer to the cookbook section 2, paragraph 3, standard sample preparation method.

(2) Stannous chloride solution (10 w/v%) :
60 m*l* of the sulfuric acid (sulfuric acid and water mixed at the volume rate of 1:20) is added to 10 g of the stannous chloride (dihydrate), mixed and dissolved by heating. After letting it cool, increased the total volume to 100 m*l* with water.

**Operation**

(1) The pretreated sample is used for measurement as it is.

(2) For the calibration curve, 2.5 to 12.5 m*l* of Hg from the Hg standard solution (0.1 μg Hg/m*l*) is taken by stages, and 20 m*l* of sulfuric acid (1+1) is added. Increase it up to 250 m*l* with water and use it for measurement.

**Measurement**

The mercury vaporizer unit MVU-1A is connected to the atomic absorption spectrophotometer to measure the sample.

Refer to the instruction manual for operation of MVU-1A.

| | | |
|---|---|---|
| Measuring wavelength | 253.7 nm | |
| Calibration curve concentration range | 1 to 5 ng/m*l* | |
| Measuring condition | Lamp current value | 4 mA |
| Slit width | 0.5 nm | |
| Lighting mode | BGC-$D_2$ | |

## 8.2 Analysis of environmental sample

**Reference**: Japanese Industrial Standard JIS K-102-1993
Testing methods for industrial waste water
Environmental standard concerning water contamination

### 8.2.1 Preservation of sample

Nitric acid is added to the sampled water, which is preserved at about pH 1.

Hydrochloric acid is added to preserve the sample at pH 1, for the sample for As testing, which does not contain an organic substance, much nitrate salt, or nitrite salt and in case of no treatment is done by sulfuric acid, nitric acid, or potassium permanganate.

### 8.2.2 Pretreatment of sample

Pretreatment is necessary in the case of the sample which has an organic substance, or the sample in which the target component exists as colloid or metallic complex even if it looks clear.

Pretreatment is done either by adding various acids to the sample for decomposition by heating, or ashing by heating.

Select a suitable method among the following pretreatment methods specified by JIS K 0102, depending on the sample condition and test type.

**a) Boil with hydrochloric acid or nitric acid.**

This is applied to the sample, which has very small organic substances and/or suspensions.

5 m*l* of nitric acid or hydrochloric acid is added per 100 m*l* of the sample. Heated and boiled for about 10 minutes.

b) **Decomposition by hydrochloric acid or nitric acid.**

This is applied to the sample containing hydroxides, oxides, sulfides, phosphates, etc.

After the sample is well mixed, a fixed amount is taken and 5 m*l* of hydrochloric acid or nitric acid is added per 100 m*l* of the sample. It is heated and concentrated until the liquid amount comes to 15 m*l*.

c) **Decomposition by nitric acid and perchloric acid**

This is applied to the sample containing an organic substance, which is not easily oxidized.

After the sample is well mixed, a fixed amount is taken and 5 to 10 m*l* of nitric acid is added.

It is heated to decompose the organic substance. Then, perchloric acid is added in the nitric acid coexistent condition and the white fume treatment is done to decompose the substance.

d) **Decomposition by nitric acid and sulfuric acid**

This is the standard decomposition method and can be applied to many types of the samples. However, this is not recommended to the atomic absorption method when directly spraying the water solution, because a lot of the sulfate is left after treatment.

The sample is shaken and mixed well. A fixed amount is taken and 5 to 10 m*l* of nitric acid is added and heated to decompose the organic substances. Then, 10 m*l* of sulfuric acid (1+1) is added and treated until the white fume comes out of the sulfuric acid that decomposes organic substances.

e) **Decomposition by ashing**

This is applied to the sample containing the metallic element, which does not volatilize at 450 to 500 °C in the electric furnace. After the sample is evaporated, dried up; the residue is heated at 450 to 500 °C, ashed, and then dissolved in the acid. On the other hand, after alkali fusion or acid fusion, it is dissolved in the acid. This method cannot be applied to the analysis of Hg, As, Se, etc. which evaporate during heating strongly.

When a chloride is contained in the sample, Pb, Zn, Fe, Sb, etc. evaporate. Therefore, it must be pretreated with sulfuric acid to evaporate chloride.

Among the above pretreatment methods, the wet decomposition method can make solution of most metallic elements without loss. However, a lot of acid is required if many organic substances are contained in the sample. The component for determination enters from the acid to make the determination difficult and makes accuracy worse. The dry decomposition method is effective for the sample, which can be easily ashed, but cannot be applied to the determination of all elements, because some elements evaporate.

The prepared sample, which is sprayed directly as it is, for measurement is acidified with hydrochloric acid or nitric acid (where possible) and the acid concentration is in the range of 0.1

to 1 mol/*l*. The pressure of large amounts of sulfuric acid or perchloric acid generally causes a negative error. Therefore, they must be completely removed from the measuring solution.

### 8.2.3 Furnace analysis method

**a) Target elements**

Cd, Cr (VI) and Pb

**b) Measuring operation**

Measurement is made by the following method.

Refer to the cookbook section 4, paragraph 7.5 measuring condition by element for the lamp lighting current value and slit width.

◦ **Cd**

**Reagent**

(1) Cd standard solution (0.01 μg Cd/m*l*) :
Refer to the cookbook section 2, paragraph 3, "Standard Sample Preparation Method".

(2) Palladium (II) nitrate solution (10 μg Pd/m*l*) :
10 m*l* of nitric acid (1+1) is added to 0.108 g of palladium (II) nitrate to dissolve it. It is increased to 500 m*l* with water. In addition, water is added to the above solution 20 m*l* to increase it to 200 m*l*.

**Operation**

(1) 15 m*l* of the pretreated samples (when 0.01 μg or more of Cd is in the sample, the sampling amount is decreased are taken in 20 m*l* flasks to prepare the sample containing no Cd standard solution and the sample with the addition of three or more stages in the range from 0.2 m*l* to 2 m*l*. Nitric acid (1+1) is added so that the acid concentration of the respective solutions is equalized, and then water is added to the marked line.

(2) The specified amount, of 100 μ*l* or more, of the sample used in #(1) above is taken in a small container, and the palladium (II) nitrate solution (10 μg Pd/m*l*) of the same volume (as the above) is added and mixed for measurement.

**Measurement**

| | |
|---|---|
| Measurement wavelength | 228.8 nm |
| Calibration curve concentration range | 0.2 to 2 ng/m*l*<br>(Standard addition method) |
| Tube | High-density graphite tube |
| Sample injection amount | 10 m*l* |
| Heating condition | Same as the furnace analysis method for Cd in paragraph 8.1.2. |

◦ **Cr(VI)**

**Reagent**

Cr standard solution (1 μg Cr/m*l*) :

Refer to the cookbook section 2, paragraph 3, "Standard sample preparation method".

**Operation**

A proper amount of the sample is taken and nitric acid is added. Then it is used for measurement as the acid solution of 0.1 to 1 mol/*l*. The sample is filtered, if the suspension is contained. 50 m*l* of the first filtrate is thrown away and the filtrate thereafter is used. When Cr (III) is contained in the sample, operation is made in the same way as in the remarks of paragraph 8.1.2 Furnace analysis method for Cr.

**Measurement**

Measurement is made in the same way as the paragraph 8.1.2 Furnace analysis method Cr.

◦ **Pb**

**Reagent**

(1) Pb standard solution (0.2 µg Pb/m*l*) :
Refer to the cookbook section 2, "Standard sample preparation method".

(2) Palladium (II) solution (10 µg Pd/m*l*) : Same as Cd.

**Operation**

(1) 15 ml each of the pretreated samples (when 0.1 µg or more of Pb is in the sample, the sampling amount is decreased to decrease the amount of Cd below 0.1 µg) are taken in 20 m*l* flasks to prepare the sample containing no Pb standard solution and the sample with the addition of three or more stages in the range from 0.1 to 2 m*l*.
Nitric acid (1+1) is added so that the acid concentration of the respective solutions is equalized. Then water is added up to the marked line.

(2) The specified amount of 100 m*l* or more of the sample used in (1) above is taken in a small container and the palladium (II) nitrate, of the same volume as the above, is added and mixed well for measurement.

**Measurement**

| | |
|---|---|
| Measurement wavelength | 283.3 nm |
| Calibration curve concentration range | 1 to 20 ng/m*l*<br>(Standard addition method) |
| Tube | High-density graphite tube |
| Sample injection amount | 20 m*l* |
| Heating condition | Same as the furnace analysis method for Cd in paragraph 8.1.2. |

### 8.2.4 Flame analysis method

#### a) Target elements

Cd, Cr(VI) and Pb

**b) Measuring operation**

Measurement is made by the following method.

Refer to the cookbook section 3, paragraph 6.4, “Measurement condition by element for the lamp current value, slit width, and flame condition”.

- **Cd I** (When the Cd concentration is in the determination range from 0.05 to 1 μg/m*l* and no interfering components are contained).

**Reagent**

Cd standard solution (10 μg Cd/m*l*) :

Refer to the cookbook section 2, paragraph 3, “Standard sample preparation method”.

**Operation**

(1) The sample pretreated in paragraph 8.2.2 is used. As the blank test, water of the same volume of the sample, is taken and pretreated in the same way as the sample.

Then, measurement is made to correct the indicated value obtained concerning the sample.

(2) For the calibration curve, 0.5 to 10 m*l* of the Cd standard solution (10 μg Cd/m*l*) is taken in the 100 m*l* flask by stages. Then, acid is added to obtain the same condition as the sample. Then water is added up to the marked line for measurement.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 228.8 nm |
| Calibration curve concentration range | 0.05 to 1 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4.11). |

- **Cd II** (When the Cd concentration is below the determination range, or the interfering component is contained, measurement is made with a water solution).

**Reagent**

(1) Cd standard solution : Same as Cd I

(2) Dithizone chloroform solution (0.1 g/*l*) :

Prepare it according to the remarks.

(3) Diammonium hydrogen citrate solution (10 g/*l*) :

10 g of diammonium hydrogen citrate is dissolved in 80 m*l* of water. Two or three drops of meta cresol purple solution (0.1 w/v%) are added and ammonia water (1+1) is added

to adjust the pH to about 9. Then it is increased to 100 m*l* with water. This is transferred to a separating funnel and 2 m*l* of sodium diethyldithiocarbanate solution (1 w/v%) and 10 m*l* of acetic acid-n-butyl (or chloroform) are added and then shaken up. Then they are kept stationary.

The diammonium hydrogen citrate layer is separated, and 10 m*l* of acetic acid-n-butyl is added again and shaken up and then is kept stationary. The diammonium hydrogen citrate layer is separated and filtered with dry filter paper to remove small bubbles of acetic acid-n-butyl.

(4) Hydrochloric acid hydroxylamine solution (10 w/v%) :

100 g of hydrochloric acid hydroxylamine is dissolved in water to accurately come to 1000 m*l*.

(5) Thymol blue solution (0.1 w/v%) :

0.1 g of thymol blue is dissolved in ethyl alcohol (852 w/v%) and it is increased to 100 m*l* with water.

(6) Hydrochloric acid, ammonia water and chloroform :

The analytical grade reagent is used.

**Operation**

(1) 10 m*l* of hydrochloric acid is added to 500 m*l* of the sample. In addition, boil it for five minutes then let it cool.

It is taken in a 1 liter separating funnel and 10 m*l* of the diammonium hydrogen citrate solution, 2 m*l* of hydrochloric acid hydroxylamine solution and two to three drops of thymol blue solution as indicator are added. Then, ammonia water (1+1) is added until the liquid turns blue. 5 m*l* is further added as surplus. 10 to 20 m*l* of dithizone chloroform solution is added and it is shaken up for two minutes. Let it stand until the chloroform layer separates, and then put it in another separating funnel.

5 m*l* of dithizone chloroform solution is added to the water layer and shaken up to extract the layer again. This extraction is repeated until the chloroform layer does not change color. The extracted chloroform layers are put together.

The layer is washed with 20 m*l* of ammonia water (1 + 100) and then, with 20 m*l* of water. The chloroform layer is separated to another separating funnel, and 20 m*l* of hydrochloric acid (1 + 50) is added and shaken up. Then let it stand until the chloroform layer separates. Then deposit into another separating funnel. Again, add 10 ml of hydrochloric acid (1+50) and shake up and then let it stand still to separate the chloroform layer.

Two back-extracted water layers are put together to come to the specified amount and are used for measurement of cadmium.

(2) For the calibration curve, the Cd standard solution is taken by stages and operates in the same way as the sample.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 228.8 nm |
| Calibration curve concentration range | 0.05 to 1 μg/m*l*<br>(Concentration in the solution after extraction) |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 11). |

**Remarks**

400 m*l* chloroform is added to 0.11 g of dithizone (1-5-diphenylthiocarbazon), mixed well, and dissolved. Then it is filtered with filter paper (5A).

This is put in the separating funnel and 400 m*l* of ammonia water (1+100) is added and shaken up to transfer the chloroform to the water layer. After it is left alone, the chloroform layer is removed. 50 m*l* of chloroform is added to the water layer and shaken up to remove the chloroform layer again.

This operation is repeated until the chloroform layer turns light green. 500 m*l* of chloroform and 50 m*l* of hydrochloric acid (1+10) are added to the water layer and shaken up to transfer dithizone to the chloroform layer. After it is left alone, the chloroform layer is put into an Erlenmeyer flask. 500 m*l* of chloroform is added to the water layer and shaken up to extract the remaining dithizone. Dithizone is put into the above Erlenmeyer flask and chloroform is added to increase it to 1 liter.

Put it in the colored bottle and add 100 m*l* of sulfurous acid (saturated) to cover the surface and preserve it below 10 °C.

◦ **Cd III** (When the Cd concentration is below the determination range or an interfering component is contained : Measurement is made with an organic solvent.)

**Reagent**

(1) Cd standard solution : Same as Cd I

(2) Diammonium hydrogen citrate solution (10 g/*l*) :
Same as the Cd II reagent (3).

(3) Meta cresol purple solution (1 g/*l*) :
0.1 g of meta cresol purple is dissolved in 50 m*l* of ethanol. Then water is added to obtain 100 m*l*.

(4) Sodium diethyldithiocarbamate solution (10 g/*l*) :

1.3 g of N, N-sodium diethyldithiocarbamate triee-hydrate is dissolved in water to obtain a 100 m*l* solution.

(5) Butyl acetate

**Operation**

(1) 10 m*l* of hydrochloric acid is added to 500 m*l* of the sample, and then the solution is boiled for 15 minutes and then cooled. This is taken in a 1-liter separating funnel and 10 m*l* of diammonium hydrogen citrate solution, and two or three drops of meta cresol purple solution are added as an indicator. Then, ammonia water (1+1) is added until the solution turns slightly purple.

5 m*l* of sodium diethyldithiocarbamate solution is added, and shaken up. Then 10 to 20 m*l* of butyl acetate is added and shaken up for one minute. Then, let it stand still. The butyl acetate layer is separated and put it in the volumetric flask. 5 m*l* of butyl acetate is added to the water layer to repeat the extraction operation. The extracted butyl acetate layer is put in the above flask. Butyl acetate is added to the extracted butyl acetate layer to obtain a specified amount to be used for the measurement of cadmium.

(2) For the calibration curve, Cd standard solution is taken by stages and operates in the same way as the sample.

**Measurement**

| | | |
|---|---|---|
| Measuring wavelength | 228.8 nm | |
| Calibration curve concentration range | 0.02 to 0.5 μg/m*l*<br>(Concentration in the solution after extraction). | |
| Measuring condition | Lamp current value | 8 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |
| | Burner height | 7 mm |
| | Oxidant | Air |
| | Fuel gas flow | $C_2H_2$ 0.8 *l*/min |
| | (Sample amount is decreased if the flame turns slightly red when sample is sprayed). | |

- **Cr(VI) I** (When the Cr concentration is in the determination range of 0.2 to 5 μg/m*l* and interfering components are not contained.)

**Reagent**

Cr standard solution (10 μg Cr/m*l*) :

Refer to the cookbook section 3, paragraph 3, Standard sample preparation method.

**Operation**

(1) A proper amount of the sample is taken. When it contains suspension, it is filtered with filter paper (5C) or filter having 0.45 μm hole diameter. At that time, 50 m*l* of the first filtrate is thrown away, and the filtrate thereafter is used. To the sample hydrochloric acid or nitric acid is added to obtain a 0.1 to 1 mol/*l* acid solution to be used for measurement.

As the blank test, water is treated in the same way as the sample, and measured to correct the indicated value obtained concerning the sample.

(2) For the calibration curve, 2 to 50 m*l* of Cr standard solution (10 μg Cr/m*l*) is taken in 100 m*l* flasks by stages. The acid, and water are added to the marked line so that the same condition as the sample is obtained.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 357.9 nm |
| Calibration curve concentration range | 0.2 to 5 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 13. |

◦ **Cr(VI) II** (When the Cr concentration is below the determination range, and Cr (III) is contained.)

**Reagent**

(1) Cr standard solution (10 μg Cr/m*l*) : Same as Cr (VI) I.

(2) Ferrous Ammonium Sulfate :

1 m*l* of sulfuric acid (1+1) and water is added to the 5 g of ferrous ammonium sulfate 12 $H_2O$ to dissolve it and the total amount is increased to 100 m*l*.

(3) Ammonium nitrate solution (10 g/*l*) :

10 g of ammonium nitrate is dissolved in water and the total amount is increased to 1 liter.

**Operation**

(1) 500 m*l*, or less of sample is taken and 1 m*l* of ferrous ammonium sulfate solution is added and shaken up.

Ammonia water (1+4) is added to be slightly alkaline. Then it is gently boiled until the odor of ammonia is nearly lost.

After it is kept near the boiling point to mature settlement, it is filtered with filter paper (5A) and washed with hot ammonium nitrate solution. The filter paper, and wash solution are put together. Hydrochloric acid or nitric acid is added to obtain a 0.1 to 1 mol/*l* acid solution.

(2) The calibration curve is the same as Cr (VI) I.

**Measurement**

Same as Cr (VI) I.

◦ **Cr(VI) III** (When the Cr concentration is below the determination range and Cr (III) is not contained.)

**Reagent**

(1) Chromium standard solution (10 μg Cr/m*l*) : Same as Cr (VI) I

(2) Potassium permanganate solution (3 g/*l*) :
0.3 g of potassium permanganate is dissolved in water to obtain 100 m*l*.

(3) N, N-dioctyloctaneamine butyl acetate solution (30 g/*l*) :
3g of N, N-dioctyloctaneamine is dissolved in butyl acetate to obtain 100 ml solution.

**Operation**

(1) A proper amount of the sample (including 5 to 100 μg of Cr) is taken in a 100 m*l* beaker. 2 m*l* of sulfuric acid (1+2) and a few drops of potassium permanganate solution are added, and the solution is heated.
Drops of potassium permanganate solution are added when the color of permanganic acid is going to disappear. Boiling is kept on for several minutes, so that the color of the solution is always slightly red.
It is cooled with flowing water and is transferred to the separating funnel.
Water is added to obtain a 100 m*l* solution. 20 m*l* of N, N-dioctyloctaneamine butyl acetate solution is added and shaken for 10 minutes. Then let it stand still. The butyl acetate layer is sprayed in the flame, and chromium is determined.

(2) For the calibration curve, Cr standard solution is taken by stages and operates them in the same way as the sample.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 357.9 nm |
| Calibration curve concentration range | 0.2 to 3 μg/m*l*<br>(Concentration in the solution after extraction) |
| Measuring condition | Lamp current value 10 mA |

| | |
|---|---|
| Slit width | 0.5 nm |
| Lighting mode | BGC-$D_2$ |
| Burner height | 9 mm |
| Oxidant | Air |
| Fuel gas flow | $C_2H_2$ 1.5 *l*/min |

◦ **Pb I** (When Pb concentration is in the determination range from 0.5 to 5 µg/m*l* and an interfering component is not contained.)

**Reagent**

Pb standard solution (10 µg Pb/m*l*) :
Refer to the cookbook section 2, paragraph 3, "Standard Sample Preparation Method".

**Operation**

(1) The sample pretreated as in paragraph 8.2.2 is used for measurement. For the blank test, water of the same volume as the sample is taken, and pretreatment is done in the same way as the sample. Concerning the sample, measurement is done to correct the indicated value obtained.

(2) For the calibration curve, 5 to 50 m*l* of Pb standard solution is taken in a 100 m*l* flask by stages, and acid is added to obtain the same condition as the sample. Then, water is added to the marked line.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 217.0 nm |
| Calibration curve concentration range | 0.5 to 5 µg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 26). |

◦ **Pb II** (When Pb concentration is below the determination range, or an interfering component is included : Measurement is made with a water solution.)

**Reagent**

(1) Pb standard solution (10 µg Pb/m*l*) : Same as Pb I reagent (1)
(2) Dithizone chloroform solution (0.03 w/v%)
(3) Diammonium hydrogen citrate solution (10 µg/*l*)
(4) Hydrochloric acid hydroxylamine solution (10 w/v%)

(5) Thymol blue solution (0.1 w/v%)
(6) Hydrochloric acid, ammonia water and chloroform.

(2), (3), (4), (5) and (6) are the same as Cd II reagent (2) through (6) in paragraph 8.2.4.

**Operation**

(1) Same as Cd II in paragraph 8.2.4.
(2) For the calibration curve Pb standard solution are taken by stages and operates them it in the same way as the sample.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 217.0 nm |
| Calibration curve concentration range | 0.5 to 5 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 26). |

◦ **Pb III** (When Pb concentration is below the determination range, or an interfering component is included : Measurement is made with organic solution).

**Reagent**

(1) Pb standard solution (10 μg Pb/m*l*) : Same as Pb I reagent (1)
(2) Diamonium hydrogen citrate solution (10 g/*l*)
(3) Meta cresol purple solution (1 g/*l*)
(4) Sodium diethyldithiocarbamate solution (10 g/*l*)
(5) Butyl acetate

(2), (3), (4) and (5) are same as Cd III reagent (2) through (5) in paragraph 8.2.4.

**Operation**

(1) Same as Cd II in paragraph 8.2.4.
(2) The calibration curve takes Pb standard solution by stages and operates in the same way as the sample.

**Measurement**

| | | |
|---|---|---|
| Measuring wavelength | 217.0 nm | |
| Calibration curve concentration range | 0.3 to 3 μg/m*l*<br>(Concentration in the solution after extraction) | |
| Measuring condition | Lamp current value | 12 mA |

| | |
|---|---|
| Slit width | 0.5 nm |
| Lighting mode | BGC-$D_2$ |
| Burner height | 7 mm |
| Oxidant | Air |
| Fuel gas flow | $C_2H_2$ 0.8 *l*/min |

(Sample suction amount is decreased when the flame turns slightly red during sample spraying.)

### 8.2.5 Hydride vapor generation analysis method

**a) Target elements**

As and Se

**b) Pretreatment of sample**

- **As**

  100 ml of the sample is taken and 1 m*l* of sulfuric acid (1+1), and 2 m*l* of nitric acid are added. Then heat it to generate white fume of sulfuric acid. After letting it cool to the room temperature, 5 m*l* of hydrochloric acid (1+1) and 5 m*l* of potassium iodide solution (200 g/*l*) are added and it is increased to 50 m*l* with water. After it is left for 15 minutes, it is used for measurement.

- **Se**

  100 m*l* of the sample is taken and operation is made in the same way as As to generate white fume of sulfuric acid. After letting it cool to the room temperature, 5 m*l* of hydrochloric acid (1+1) is added and it is increased to 50 m*l* with water to be used for measurement.

**c) Measuring operation**

Operation is made in the same way as the hydride vapor generation analysis method c) Measuring operation in paragraph 8.1.3.

### 8.2.6 Mercury reduction vapor atomization method

**a) Target elements**

Total Hg

**b) Pretreatment of sample**

Operation is made in the same way as the Mercury reduction vapor atomization method b) Pretreatment of sample in paragraph 8.1.4.

**c) Measuring operation**

Operation is made in the same way as the Mercury reduction vapor atomization method c) Measuring operation in paragraph 8.1.4.

## 8.3 Analysis of wastewater

**References**: Japanese Industrial Standard JIS K 0102-1993, “Testing Methods for Industrial Water Testing Methods Specified by Director General of the Environment Agency Concerning Waste Water Quality Standards”

### 8.3.1 Preservation of sample

It is done in the same way as sample preservation in paragraph 8.2.1.

### 8.3.2 Pretreatment of sample

It is done in the same way as sample pretreatment in paragraph 8.2.2.

### 8.3.3 Furnace analysis method

**a) Target elements**

Cd, Cr (VI), total Cr, Cu, Fe, Mn, Pb and Zn

**b) Measuring operation**

Measurement is made by the following methods: Refer to the cookbook section 4, paragraph 7.5, “Measuring Condition by Element for the Lamp Lighting Current Value and Slit Width”.

- **Cd**

  Same analysis method as furnace analysis method for Cd in paragraph 8.2.3.

- **Cr (VI)**

  Same analysis method as furnace analysis method for Cr (VI) in paragraph 8.2.3.

- **Total Cr**

  **Reagent**

  Cr standard solution (1 µg Cr/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

  **Operation**

  The pretreated sample is used for measurement as it is.

  **Measurement**

Measurement is made in the same way as the furnace analysis method for Cr (VI) in paragraph 8.2.3.

- **Cu**

  **Reagent**

  Cu standard solution (1 µg Cu/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

  **Operation**

  The pretreated sample is used for measurement as it is.

  **Measurement**

  Measurement is made in the same way as the furnace analysis method for Cu in paragraph 8.1.2.

- **Fe**

  **Reagent**

  Fe standard solution (1 µg Fe/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

  **Operation**

  The pretreated sample is used for measurement as it is.

  **Measurement**

  Measurement is made in the same way as the furnace analysis method for Fe in paragraph 8.1.2.

- **Mn**

  **Reagent**

  Mn standard solution (1 µg Mn/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

  **Operation**

  The pretreated sample is used for measurement as it is.

  **Measurement**

  Measurement is made in the same way as the furnace analysis method for Mn in paragraph 8.1.2.

- **Pb**

  Same analysis method as furnace analysis method for Pb in paragraph 8.2.3.

- **Zn**

  **Reagent**

  Zn standard solution (0.1 μg Zn/m*l*) :

  Refer to the cookbook section 2, paragraph 3, "Standard Sample Preparation Method".

  **Operation**

  The pretreated sample is used for measurement as it is.

  **Measurement**

  Measurement is made in the same way as the furnace analysis method for Zn in paragraph 8.1.2.

### 8.3.4 Flame analysis method

**a) Target elements**

Cd, Cr (VI), total Cr, Cu, Fe, Mn, Pb and Zn

**b) Measuring operation**

Measurement is made by the following methods.

Refer to the cookbook section 3, paragraph 6.4, "Measuring condition by element" for the lamp current value, slit width and flame conditions.

- **Cd I** (When Cd concentration is in the determination range from 0.05 to 1 μg/m*l* and interfering component is not included).

  The same analysis method as the flame analysis method for Cd I in paragraph 8.2.4.

- **Cd II** (When Cd concentration is below the determination range, or an interfering component is included : Measurement is made with a water solution.)

  The same analysis method as the flame analysis method for Cd II in paragraph 8.2.4.

- **Cd III** (When Cd concentration is below the determination range or interfering component is included : Measurement is made with organic solvent.)

  The same analysis method as the flame analysis method Cd III in paragraph 8.2.4.

- **Cr (VI) I** (When Cr concentration is in the determination range from 0.2 to 5 μg/m*l* and an interfering component is not included).

  The same analysis method as the flame analysis method for Cr (VI) I in paragraph 8.2.4.

- **Cr (VI) II** (When Cr concentration is below the determination range and chromium (III) is included).

  The same analysis method as the flame analysis method for Cr (VI) II in paragraph 8.2.4.

- **Cr (VI) III** (When Cr concentration is below the determination range and chromium (III) is not included.)

  The same analysis method as the flame analysis method for Cr (VI) III in paragraph 8.2.4.

- **Total Cr I** (When Cr concentration is in the determination range from 0.2 to 5 μg/m*l* and an interfering component is not included).

  **Reagent**

  Cr standard solution (10 μg Cr/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

  **Operation**

  (1) The sample pretreated in paragraph 8.2.2 is used for measurement. As a blank test, water of the same volume as the sample is taken and pretreated in the same way as the sample. It is measured to correct the indicated value obtained concerning the sample.

  (2) For the calibration curve 2 to 50 m*l* of Cr standard solution (10 μg Cr/m*l*) are taken in a 100 m*l* flask by stages and the acid is added to obtain the same condition as the sample. Then water is added to the marked line, and used for measurement.

  **Measurement**

  Measurement is made in the same way as flame analysis method for Cr (VI) I in paragraph 8.2.4.

- **Total Cr II** (When Cr concentration is below the determination range, or an interfering component is included).

  The same analysis method as the Flame analysis method for Cr (VI) II in paragraph 8.2.4.

- **Cu I** (When Cu concentration is in the determination range from 0.2 to 4 μg Cu/m*l* and an interfering component is not included).

  **Reagent**

  Cu standard solution (10 μg Cu/m*l*) :

  Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

1. (1) The sample pretreated in paragraph 8.2.2 is used for measurement. As a blank test, water of the same volume as the sample is taken and pretreated in the same way as the sample. It is measured to correct the indicated value obtained concerning the sample.
2. (2) For the calibration curve, 2 to 40 m*l* of Cu standard solution (10 μg Cu/m*l*) is taken in a 100 m*l* flask by stages and the acid is added to obtain the same condition as the sample. Then water is added to the marked line to be used for measurement.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 324.7 nm |
| Calibration curve concentration range | 0.2 to 4 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 15. |

◦ **Cu II** (When Cu concentration is below the determination range, or an interfering component is included : Measurement is made with water solution.)

**Reagent**

(1) Cu standard solution (10 μg Cu/m*l*) : Same as Cu I.

(2) Dithizone chloroform solution (0.1 g/*l*) :
Same as Cd II reagent (2) in paragraph 8.2.4.

(3) Hydrochloric acid, phosphoric acid, nitric acid and perchloric acid (60%) : Analytical grade reagent is used.

**Operation**

(1) 500 m*l* of the sample is taken in a beaker and 5 m*l* of hydrochloric acid and 2 m*l* of phosphoric acid are added, and boiled for 5 minutes. After letting it cool, it is transferred to a 1-liter separating funnel and 10 m*l* of dithizone chloroform solution is added and shaken up for one minute.

After letting it stand still, the chloroform layer is separated and transferred to the beaker. Another 5 m*l* of dithizone chloroform is added to aqueous lager and extract. This extraction operation is repeated until the chloroform layer does not change color.

The extracted chloroform layer is put in the above beaker. After the chloroform layer is evaporated by heating, 2 m*l* of nitric acid and 2 m*l* of perchloric acid are added and heated to decompose organic substances. After it is almost dried up, let it cool. The residue is dissolved in 10 m*l* of nitric acid (1+15) and is used for measurement.

(2) The calibration curve is same as Cu I.

**Measurement**

Same as Cu I.

◦ **Cu III** (When Cu concentration is below the determination range, or an interfering component is included : Measurement is made with an organic solvent.)

**Reagent**

(1) Cu standard solution (10 μg Cu/m*l*) : Same as Cu I.
(2) Diammonium hydrogen citrate solution (10 g/*l*) :
Same as Cd I reagent (3) in paragraph 8.2.4.
(3) Meta cresol purple solution (1 g/*l*)
(4) Sodium diethyldithiocarbamate solution (10 g/*l*).
(5) Butyl acetate

(3), (4) and (5) are same as Cd reagent (3) through (5) in paragraph 8.2.4.

**Operation**

(1) Same as Cd III in paragraph 8.2.4
(2) For the calibration curve, Cu standard solution is taken by stages, and operates them in the same way as the sample.

**Measurement**

| | | |
|---|---|---|
| Measuring wavelength | 324.7 nm | |
| Calibration curve concentration range | 0.1 to 2 μg/m*l*<br>(Concentration in the solution after extraction) | |
| Measuring condition | Lamp current value | 6 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |
| | Burner height | 7 mm |
| | Oxidant | Air |
| | Fuel gas flow | $C_2H_2$ 0.8 *l*/min |

(Sample suction amount is decreased when flame turns slightly red during sample spraying).

◦ **Fe I** (When Fe concentration is in the determination range from 0.3 to 6 μg Cu/m*l* and an interfering component is not included).

**Reagent**

Fe standard solution (10 μg Fe/m*l*) : Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

(1) The sample pretreated in paragraph 8.2.2 is used for measurement. As a blank test, water of the same volume as the sample is taken and pretreated in the same way as the sample. It is measured to correct the indicated value obtained concerning the sample.

(2) For the calibration curve, 3 to 60 m*l* of Fe standard solution (10 μg Fe/m*l*) are taken in a 100 m*l* flask by stages and the acid is added to obtain the same condition as the sample. Then water is added to the marked line to be used for measurement.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 248.3 nm |
| Calibration curve concentration range | 0.3 to 6 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 16. |

◦ **Fe II** (When Fe concentration is below the determination range, and an interfering substance is barely traceable).

**Reagent**

(1) Fe standard solution (10 μg Fe/m*l*) : Same as Fe I.

(2) Nitric acid, ammonia water and hydrochloric acid : analytical grade reagents are used.

**Operation**

(1) 200 m*l* of the sample is taken in a breaker and 2 m*l* of nitric acid is added and boiled. Then ammonia water (1+1) is added, to be slightly alkaline. It is boiled for several minutes to generate precipitation, and let it stand still for a while. After precipitation settles down, it is filtered with filter paper (5A) and washed several times with hot water. The precipitation is put in the above beaker and 4 m*l* of hydrochloric acid (1+1) is added, and heated to dissolve it. It is filtered with the above filter paper and at the same time, iron hydroxide attached to the filter paper is dissolved. The filter paper is washed several times with hot water. Filtrate and wash liquid are put together, heated and concentrated to 20 m*l*. It is then used for measurement.

(2) The calibration curve is the same as Fe I.

**Measurement**

Same as Fe I.

◦ **Mn I** (When Mn concentration is in the determination range from 0.2 to 3 μg/m*l* and an interfering component is not included).

**Reagent**

Mn standard solution (10 μg Mn/m*l*) :

Refer to the cookbook section 2, paragraph 3 Standard sample preparation method.

**Operation**

(1) The sample pretreated in paragraph 8.2.2 is used for measurement. As a blank test, water of the same volume as the sample is taken and pretreated in the same way as the sample. It is measured to correct the indicated value obtained concerning the sample.

(2) For the calibration curve, 2 to 30 m*l* of Mn standard solution (10 μg Mn/m*l*) is taken in a 100 m*l* flask by stages and the acid is added to obtain the same condition as the sample. Then water is added to the marked line to be used for measurement.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 279.5 nm |
| Calibration curve concentration range | 0.2 to 3 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 22. |

◦ **Mn II** (When Mn concentration is below the determination range :
Measurement is made with a water solution)

**Reagent**

(1) Mn standard solution (10 μg Mn/m*l*) : Same as Mn I.

(2) Ferrous ammonium sulfate (III) solution (2 m Fe/m*l*) :
1.8 g of ammonium sulfide (III) 12 $H_2O$ is taken and 10 m*l* of nitric acid (1+6) is added to dissolve it. Water is added to increase it to 100 m*l*.

(3) Nitric acid, hydrogen peroxide, ammonia water (1+1) and sulfuric acid : Analytical grade reagent is used.

**Operation**

(1) A proper amount of the sample, less than 500 m*l*, is taken in a beaker. It is heated at 90 °C. 5 m*l* of ferrous ammonium sulfate solution, and 5 to 10 m*l* of hydrogen peroxide (30%) is added. This solution is stirred and ammonia water (1+1) is added to generate a precipitation of iron hydroxide.

After precipitation settles down, it is filtered with filter paper (5A) and washed with hot water.

As much as possible of the precipitation is transferred to the above beaker.

Precipitation attached to the filter paper is dissolved in a small amount of hydrochloric acid (1+2) added with a small amount of hydrogen peroxide water (1+10).

The filter paper and wash liquid are put in the above beaker, heated and concentrated to 20 ml to be used. This solution is 0.1 to 1 mol/*l* hydrochloric acid.

(2) For the calibration curve, Mn standard solution is taken by stages and operates them in the same way as the sample.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 279.5 nm |
| Calibration curve concentration range | 0.2 to 3 µg/m*l*<br>(Concentration after separation and concentration) |
| Measuring condition | Same as Mn I |

◦ **Mn III** (When Mn concentration is below the determination range : Measurement is made with organic solvent)

**Reagent**

(1) Mn standard solution (10 µg Mn/m*l*) : Same as Mn I.

(2) Ammonium sulfide solution (saturated)

(3) 1-ammonium pyrrolidinedithiocarbamate solution (10 g/*l*) :

1 g of pyrrolidine-N-dithiocarbamido acid (APDC) is dissolved in water and it is increased to 100 m*l*.

(4) 4-methyl-2-pentanone (MIBK) : Analytical grade reagent is used.

**Operation**

(1) 200 m*l* of the sample is taken in a breaker and 5 m*l* of hydrochloric acid is added and boiled for 5 minutes. The pH is adjusted from 3.5 to 4.0, the solution is transferred to a 300 ml separating funnel, and ammonium sulfide solution is added. Then, 5 m*l* of 1-ammonium pyrrolidinedithiocarbamate solution is added and shaken gently and then left for 3 minutes. 10 m*l* of 4-methyl-2-pentanone is added and shaken up for 3 minutes. The organic layer and water are completely separated, and the organic layer is used for measurement.

(2) For the calibration curve, Mn standard solution is taken by stages and operates them in the same way as the sample.

**Measurement**

| | | |
|---|---|---|
| Measuring wavelength | 279.5 nm | |
| Calibration curve concentration range | 0.1 to 2 μg/m*l*<br>(Concentration in the solution after extraction) | |
| Measuring condition | Lamp current value | 10 mA |
| | Slit width | 0.2 nm |
| | Lighting mode | BGC-$D_2$ |
| | Burner height | 7 mm |
| | Oxidant | Air |
| | Fuel gas flow | $C_2H_2$ 0.8 *l*/min |

(Sample suction amount is decreased when flame turns slightly red during sample spraying).

◦ **Pb I** (When Pb concentration is in the determination range from 0.5 to 5 μg/m*l* and an interfering component is not included.)

Same analysis method as flame analysis method for Pb I in paragraph 8.2.4.

◦ **Pb II** (When Pb concentration is below the determination range or an interfering component is included : Measurement is made with water solution).

Same analysis method as flame analysis method for Pb II in paragraph 8.2.4.

◦ **Pb III** (When Pb concentration is below the determination range or an interfering component is included : Measurement is made with an organic solvent).

Same analysis method as flame analysis method for Pb III in paragraph 8.2.4.

◦ **Zn I** (When Zn concentration is in the determination range from 0.05 to 1 μg/m*l* and an interfering component is not included.)

**Reagent**

Zn standard solution (10 μg Zn/m*l*) :

Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

(1) The sample pretreated in paragraph 8.2.2 is used for measurement. As a blank test, water of the same volume as the sample is taken and pretreated in the same way as the sample. Then, measurement is made to correct the indicated value obtained concerning the sample.

(2) For the calibration curve, 0.5 to 10 m*l* of Zn standard solution (10 μg Zn/m*l*) is taken in a 100 m*l* flask by stages. The acid is added to obtain the same condition as the sample.

Then, water is added to the marked line and the solution is used.

**Measurement**

| | |
|---|---|
| Measuring wavelength | 213.9 nm |
| Calibration curve concentration range | 0.05 to 1 μg/m*l* |
| Measuring condition | Refer to the cookbook section 3, paragraph 6.4 44). |

- **Zn II** (When Zn concentration is below the determination range or an interfering component is included : Measurement is made with water solution).

**Reagent**

(1) Zn standard solution (10 μg Zn/m*l*) ; Same as Zn I.
(2) Dithizone chloroform solution (10 g/*l*).
(3) Diammonium hydrogen citrate solution (0.1 g/*l*).
(4) Hydrochloric acid hydroxylamine solution (10 w/v%).
(5) Thymol blue solution (0.1 w/v%).
(6) Hydrochloric acid, ammonia water and chloroform

(2), (3), (4), (5) and (6) are the same as Cd II reagent (2) through (6) in paragraph 8.2.4.

**Operation**

(1) Same as Cd II in paragraph 8.2.4.
(2) For the calibration curve, Zn standard solution is taken by stages and operates them in the same way as the sample.

**Measurement**

Same as Zn I.

- **Zn III** (When Zn concentration is below the determination range or an interfering component is included : Measurement is made with an organic solvent).

**Reagent**

(1) Zn standard solution (10 μg Zn/m*l*) : Same as Zn I.
(2) Diammonium hydrogen citrate solution (0.1 g/*l*) :
Same as Cd II reagent (3) in paragraph 8.2.4.
(3) Meta cresol purple solution (1 g/*l*)
(4) Sodium diethyldithiocarbamate solution (10 g/*l*).

(5) Butyl acetate

(3), (4) and (5) are the same as Cd III reagent (3) through (5) in paragraph 8.2.4.

**Operation**

(1) Same as Cd III in paragraph 8.2.4.

(2) For the calibration curve, Zn standard solution is taken by stages and operates them in the same way as the sample.

**Measurement**

| | | |
|---|---|---|
| Measuring wavelength | 213.9 nm | |
| Calibration curve concentration range | 0.02 to 0.5 µg/m*l*<br>(Concentration in the solution after extraction.) | |
| Measuring condition | Lamp current value | 8 mA |
| | Slit width | 0.5 nm |
| | Lighting mode | BGC-$D_2$ |
| | Burner height | 7 mm |
| | Oxidant | Air |
| | Fuel gas flow | $C_2H_2$ 0.8 *l*/min |
| | (Sample suction amount is decreased when flame turns slightly red during sample spraying.) | |

8.3.5 Hydride vapor generation analysis method

a) Target elements

As and Se

**b) Pretreatment of sample**

- **As**

  Same as hydride vapor generation analysis method (b) sample pretreatment • As in paragraph 8.2.5.

- Se

  Same as hydride vapor generation analysis method (b) sample pretreatment • Se in paragraph 8.2.5.

c) Measuring operation

Operation is made in the same way as hydride vapor generation analysis method (c) measuring operation in paragraph 8.1.3.

8.3.6 Mercury reduction vapor atomization method

**a) Target elements**

Total Hg

**b)** **Pretreatment of sample**

Operation is made in the same way as mercury reduction vapor atomization method (b) sample pretreatment in paragraph 8.1.4.

**c)** **Measuring operation**

Operation is made in the same way as mercury reduction vapor atomization method (c) measuring operation in paragraph 8.1.4.

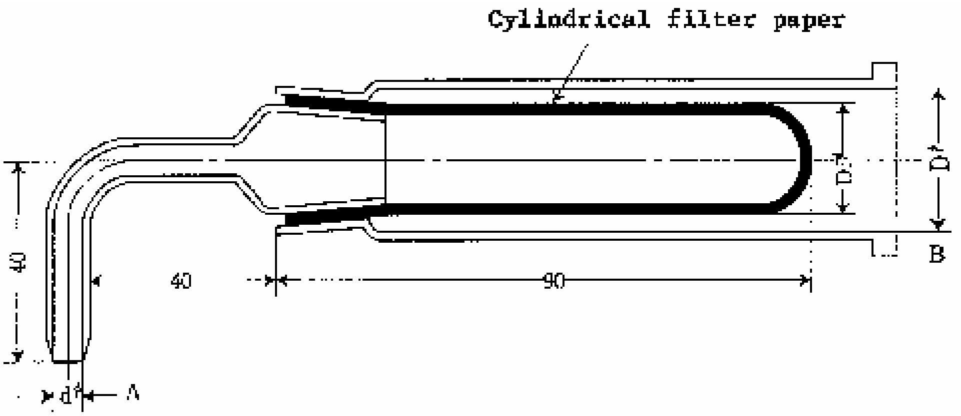
# 9. Air analysis

## 9.1 Analysis of exhaust gas

| **References**: | Japanese Industrial Standard | |
|---|---|---|
| | Analysis of exhaust gas | JIS Z-8808 |
| | | K-0095 |
| | | K-0096 |
| | | K-0097 |

### 9.1.1 Sampling

The end of the sample catcher shown in the figure is connected to the exhaust source, and the D end is connected to the suction pump to collect the air. (Refer to JIS Z-8808 for details of the suction method). The following types of cylindrical filter paper for collecting the sample are selectively used depending on temperature of exhaust gas as shown in the table.



Example of dimensions Unit mm

| | |
|---|---|
| D | 24, 36 |
| d | 4, 6, 8, 10, 12, 14, 16 |
| Df | 20, 25, 28 |

**Figure**: Hard glass or quartz glass sample catcher (When the cylindrical filter paper holder Df = 25 mm is used).

Table exhausts gas temperature and filter paper types:

| Temperature of exhaust gas | Type of cylindrical filter paper |
|---|---|
| 120 °C or lower | Cellulose fiber cylindrical filter paper |
| 500 °C or lower | Glass fiber cylindrical filter paper |
| 1000 °C or lower | Quartz fiber cylindrical filter paper |

Metal concentration in exhaust gas is expressed in mg of metal in 1 cubic meter of dry exhaust gas converted to the standard condition (Temperature 0 °C and air pressure 760 mm/Hg), and it is calculated by the following formula. Exhaust gas sampling amount is adjusted depending on the metal concentration in the gas.

$$C = \frac{m \times 10^3}{Q}$$

Where C : Metal concentration (mg/Nm$^3$)

m : Metal amount (mg)

Q : Dry sample gas volume in the standard condition (*l*)

### 9.1.2 Target elements

Cd, Cr, Mn and Pb

### 9.1.3 Pretreatment of sample

- **Cd and Pb**

The filter paper attached with the sample is cut into a proper size and put in a 250 m*l* round bottom flask. 60 m*l* of nitric acid (1+1) and 10 m*l* of hydrogen peroxide water (30%) are added, and an Allihn condenser is fitted. Then, the solution is heated by reflux for 1 to 2 hours in the water bath.

During this operation, 10 m*l* of hydrogen peroxide (30%) is added twice. After cooling, the Allihn condenser is washed with water, which is put with the sample solution. This solution is filtered by decantation by using the filter paper (5A).

30 m*l* of hot water is added to the above flask. Then the solution is heated for 5 to 10 minutes on the water bath, and filtered with the filter paper.

This washing is repeated several times.

The filter paper is washed with hot nitric acid (2+98). Then, filtrate and wash liquid are put together, heated, and evaporated in the water bath. It is concentrated to the extent of not being dried up. 10 m*l* of nitric acid (2+98) is added to the above, heated, and dissolved on the water bath. After cooling, it is transferred to the 250 m*l* measuring flask, and nitric acid (1+20) is added to the marked line.

Another filter paper is operated in the same way to obtain the blank solution.

- **Cr**

  The filter paper attached with the sample is ashed at 500 °C using an electric furnace. It is transferred to a platinum crucible and several drops of sulfuric acid (1+3) and 20 m*l* of hydrofluoric acid are added. Then, it is heated on the heated plate, little by little, until a white fume of sulfuric acid begins to appear. Let it cool, then 5 m*l* of hydro-fluoric acid is added and it is heated until a white fume of sulfuric acid is hardly seen. Then let it cool. Add 2 g of sodium carbonate and 0.1 g of sodium nitrate, and put the lid on. Then raise the temperature to 900 °C. The crucible is shaken from time to time to mix the contents.

  It is heated for 20 minutes and fused.

  After letting it cool, a small amount of hot water is added to the crucible and the melt is transferred to the 200 m*l* beaker. 2 m*l* of nitric acid (1+1) is added to the platinum crucible to fuse completely the attached melt and then the melt is transferred to the above beaker. At the same time, the lid of the platinum crucible is also washed with water, and wash liquid is put together. The beaker is covered with a watch glass and 8 m*l* of nitric acid (1+1) and one drop of hydrogen peroxide water (30%) are added. It is boiled to expel carbon dioxide and to be completely dissolved. After letting it cool, transfer it to a 50 m*l* measuring flask and add water to it to the marked line.

  Another filter paper is operated in the same way to obtain a blank test solution.

- **Mn**

  The filter paper, attached with the sample, is ashed at 500 °C by using an electric furnace. It is put in a 250 m*l* beaker, and 30 m*l* of hydrochloric acid and 5 m*l* of hydrogen peroxide water (30%) are added.

  Then, it is heated for 30 minutes on a water bath to decompose the filter. 10 m*l* of water is added to cool the solution. This solution is filtered by decantation using the filter paper (5A). 30 m*l* of hydrochloric acid (2+98) is added to the above beaker and the solution is heated for 5 to 10 minutes on a water bath and is filtered with the above filter paper. This washing is repeated several times. The filter paper is washed with hot hydrochloric acid. The filter paper and wash liquid are put together to the fixed amount.

Another filter paper is operated in the same way to obtain a blank test solution.

### 9.1.4 Measuring operation

◦ **Cd I** (When Cd concentration is in the determination range from 0.05 to 1 μg/m*l* and an interfering component is not included).

**Reagent**

Cd standard solution (10 μg Cd/m*l*) :

Refer to the cookbook section 2, paragraph 3, Standard sample preparation method).

**Operation**

(1) The pretreated sample and blank test solution are used for measurement as they are.

(2) For the calibration curve, 0.5 to 10 m*l* of Cadmium standard solution (10 μg Cd/m*l*) is taken in a 100 m*l* flask by stages. The acid is added to obtain the same condition as the sample.

Then, water is added to the marked line before it is used.

**Measurement**

Same as flame analysis method Cd I in paragraph 8.2.4.

◦ **Cd II** (When Cd concentration is below the determination range or an interfering component is included : Measurement is made with a water solution).

Same analysis method as flame analysis method Cd II in paragraph 8.2.4.

◦ **Cd III** (When Cd concentration is below the determination range or an interfering component is included: Measurement is made with an organic solvent).

Same analysis method as flame analysis method Cd III in paragraph 8.2.4.

◦ **Cr I** (When Cr concentration is in the determination range from 0.2 to 5 μg/m*l*).

**Reagent**

Cr standard solution (10 μg Cr/m*l*) :

Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

(1) The pretreated sample and blank test solution are used for measurement as they are.

(2) For the calibration curve, 2 to 50 m*l* of Cr standard solution (10 μg Cr/m*l*) is taken in a 100 m*l* flask by stages, and the acid is added to obtain the same condition as the sample. Then, water is added to the marked line and it is used.

**Measurement**

Same as flame analysis method Cr (VI) I in paragraph 8.2.4.

**Remarks**

When Fe, Ni, Mo, Si, Al, Ti or other interferences exists, a strontium chloride solution is added, when the sample solution is prepared to obtain 200 μg/m*l* of Sr.

◦ **Cr II** (When Cr concentration is below the determination range: Measurement is made with a water solution).

**Reagent**

(1) Cr standard solution (10 μg Cr/m*l*) : Same as Cr I.

(2) Diammonium hydrogen citrate solution (10 w/v%) : Same as flame analysis method Cd II reagent (3) in paragraph 8.2.4.

(3) Sodium diethyldithiocarbamate solution (10 g/*l*) : Same as flame analysis method Cd III reagent (4) in paragraph 8.2.4.

(4) Ammonia water, nitric acid and butyl acetate.

**Operation**

(1) A proper amount of the pretreated sample solution (containing 2 to 100 g of Cr) is taken in a 200 m*l* separating funnel, and 10 m*l* of diammonium hydrogen citrate is added. Then, ammonia water (1+1) is added to obtain a pH of 3.5 by checking pH test paper. Water is added to increase it to 100 m*l*. 5 m*l* of sodium diethydithiocarbamate solution is added and shaken up. Water is added to increase to 100 m*l*. 10 m*l* of butyl acetate is added and the solution is shaken up. Then let it stand still to separate the butyl acetate layer. After the butyl acetate layer is heated and evaporated, 10 m*l* of nitric acid (1+10) is added to evaporate and dry it up on the water bath.

After letting it cool, 10 m*l* of nitric acid (2+98) is added to dissolve it. Water is added to obtain 20 m*l*, the regular volume to be used for measurement.

Operation is made in the same way by using the blank test solution to correct the result.

(2) For the calibration curve, Cr standard solution is taken by stages and operates in the same way as the sample.

**Measurement**

Same as flame analysis method Cr (VI) I in paragraph 8.2.4.

◦ **Cr III** (When Cr concentration is below the determination range : Measurement is made with an organic solvent.)

Same analysis method as flame analysis method Cr (VI) III in paragraph 8.2.4.

◦ **Mn I** (When Mn concentration is in the determination range from 0.2 to 3 µg/m*l*).

**Reagent**

Mn standard solution (10 µg Mn/m*l*) :

Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

(1) The pretreated sample and blank test solution are used for measurement as they are.

(2) For the calibration curve, 2 to 30 m*l* of Mn standard solution (10 µg Mn/m*l*) is taken in a 100 m*l* flask by stages. The acid is added to obtain the same condition as the sample. Then, water is added to the marked line and it is used.

**Measurement**

Same as flame analysis method Mn I in paragraph 8.2.4.

◦ **Mn II** (When Mn concentration is below the determination range: Measurement is made with an organic solvent.)

**Reagent**

(1) Mn standard solution (10 µg Mn/m*l*) : Same as Mn I.

(2) Diammonium hydrogen citrate solution (10 w/v%) :
Same as flame analysis method Cd III reagent (3)in paragraph 8.2.4.

(3) Sodium diethyldithiocarbamate solution (10 g/*l*) :
Same as flame analysis method Cd III reagent (4) in paragraph 8.2.4.

(4) Ammonia water and butyl acetate.

**Operation**

(1) A proper amount of the pretreated sample solution (including 1 to 50 µg as Mn) is taken in the separating funnel and 10 m*l* of diammonium hydrogen citrate is added. Then, ammonia water (1+1) is added to obtain a pH of 3.5 by checking pH test paper. Water is added to obtain 100 m*l* solution. 5 m*l* of sodium diethydithiocarbamate solution is added and shaken up. Then, 10 m*l* of butyl acetate is added and shaken up for 1 minute. After letting it stand still, the separated butyl acetate layer is used for measurement.

(2) For the calibration curve, Mn standard solution is taken by stages and is operated in the same way as the sample.

**Measurement**

Same as flame analysis method Mn III in paragraph 8.3.4.

◦ **Pb I** (When Pb concentration is in the determination range from 0.5 to 5 µg/m*l* and interfering component is not included).

**Reagent**

Pb standard solution (10 µg Pb/m*l*) :
Refer to the cookbook section 2, paragraph 3, “Standard Sample Preparation Method”.

**Operation**

(1) The pretreated sample and blank test solution are used for measurement as they are.

(2) For the calibration curve, 5 to 50 m*l* of Pb standard solution (10 µg Pb/m*l*) is taken in a 100 m*l* flask by stages and the acid is added to obtain the same condition as the sample.
Then, water is added to the marked line then used.

**Measurement**

Same as flame analysis method Cd I in paragraph 8.2.4.

- **Pb II** (When Pb concentration is below the determination range or an interfering component is included: Measurement is made with a water solution).

Same analysis method as flame analysis method Pb II in paragraph 8.2.4.

- **Pb III** (When Pb concentration is below the determination range or an interfering component is included: Measurement is made with an organic solvent).

Same analysis method as flame analysis method Cd III in paragraph 8.2.4.

## 9.2 Analysis of air dust

**Reference**: Comment on sanitary testing methods
Edited by Japan Pharmacologists Association
Published by Kanehara Publishing Company

### 9.2.1 Sampling

Glass fiber filter paper is left for 1 day in an air-conditioned room at temperature 24 °C with humidity at 50% and weighed as constant weight. This filter paper is fitted to the high volume air sampler with shelter to collect air for 1 to 24 hours at the suction speed of $1.5m^3$/min. The collected sample is left for one or two days in the above air-conditioned room and weighed as constant weight. Concentration of the suspended particulate matter is obtained from weight differences before and after, and collected air volume in $\mu g/m^3$.

### 9.2.2 Target elements

Cd and Pb

### 9.2.3 Pretreatment of sample

Filter paper is cut into a proper size and put in a 250 m*l* beaker. 100 m*l* of nitric acid (1+6) is added. Then, it is heated for 1 to 2 hours on a water bath.

After it is cooled, water is added to obtain a 200 m*l* solution. It is filtered, and 100 m*l* of filtrate is taken as an analysis sample. When organic substances are contained in the sample, the above operation is done after the filter paper is ashed at 400 °C or a lower temperature.

Operation is made in the same way concerning the filter paper, which does not collect the sample to obtain the blank test solution.

### 9.2.4 Measuring operation

- **Cd I** (When Cd concentration is in the determination range from 0.05 to 1 μg/m*l* and no interfering components are included.)

  Same analysis method as measuring operation for Cd I in paragraph 9.1.4.

- **Cd II** (When Cd concentration is below the determination range or an interfering component is included : Measurement is made with a water solution).

  Same analysis method as flame analysis method for Cd II in paragraph 8.2.4.

- **Cd III** (When Cd concentration is below the determination range or an interfering component is included : Measurement is made with an organic solvent.)

  Same analysis method as flame analysis method for Cd III in paragraph 8.2.4.

- **Pb I** (When Pb concentration is in the determination range from 0.5 to 5 μg/m*l* and interfering components are not included.)

  Same analysis method as measuring operation for Pb I in paragraph 9.1.4.

- **Pb II** (When Pb concentration is below the determination range or an interfering component is included : Measurement is made with a water solution.)

  Same analysis method as flame analysis method for Pb II in paragraph 8.2.4.

- **Pb III** (When Pb concentration is below the determination range or an interfering component is included : Measurement is made with an organic solvent.)

  Same analysis method as flame analysis method for Pb III in paragraph 8.2.4.

# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 6

### Foodstuffs Analysis

### Fertilizer and Feed Analysis

SHIMADZU CORPORATION
KYOTO, JAPAN

## Atomic Absorption Analysis Cookbook

## Section 6

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## G10. foodstuffs analysis

### 10.1 Vegetables, Fruits Analysis Method

Reference materials:

Health Testing Methods Commentary, Japan Pharmaceutical Society Publication, Kanehara Publishing Co.,

Foodstuffs Analysis Methods, Japan Foodstuffs Manufacturing Society, Foodstuffs Analysis Methods Editorial Commission Publication (Korin Co.)

#### 10.1.1 Sample Pretreatment

a) Nitric acid, perchloric acid decomposition

First, grind and air dry 2 ~ 5g of sample and place in a conical beaker. Wet with water, add 25 ml of nitric acid, and after mixing, set aside. Next, gently heat to start a sample reaction. After cooling, add 10 ml of perchloric acid and gently heat to concentrate. Midways, if the contained material becomes dark, add 2~3 ml portions of nitric acid and continue heating. When the contained material turns yellowish or colorless, decomposition is complete. After cooling, add 2 ml of hydrochloric acid, and use water to prepare fixed volumes of measurement solution.

Remarks:

1) If during the decomposition process the sample becomes carbonized and hardens, it will certainly explode, so be sure that nitric acid is always present in the sample while heating.
2) Measurement is suitable for As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Sb, Sn, Zn, etc., but if halogens are coexistent with As, Sb, Se and Sn, or if the contained material becomes carbonized, volatilization and loss will occur.
3) Since there is a possibility of contamination with impurities to reagents and utensils, prepare processed blank test solutions in the same way as the samples.

b) Ashing by drying

First, grind and air dry 5~10g of sample and place in a quartz beaker. Then gently heat on a hot plate. Continue heating until enough water is driven off for partial carbonization to occur. Then place the beaker in an electrical furnace, and increase the heat at a rate of 100°C per 1 hour. Then heat at 500°C for several hours to conduct ashing. If ashing is incomplete, wet with 2~5 ml of a 50% magnesium nitrate solution or nitric acid (1+1). After drying, continue ashing. Add 2~4 ml of water to the ash, and after drying, add 5 ml of hydrochloric acid to dissolve the salts. Use water to prepare fixed volumes of measurement solution.

Remarks:

There is a possibility of volatilizing almost all of the elements, with Cd being volatilized during ashing above 500°C. If halogens are coexistent, As, Sb, Sn Zn, etc. will be volatilized. Heating above 550°C will greatly reduce the element collection rate.

### 10.1.2 Electrical Heating Atomic Absorption Method

a) Target elements

Cd, Pb

b) Measurement procedure

Measurement is conducted using the following procedure. The lamp current value, and the slit width used are in accordance with Cookbook Section 4, item 7.5 Element Specific Measurement Conditions.

- Cd

Reagents:

1) Cd standard solution (0.01 µg Cd/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Palladium nitrate (II) solution (10 µg Pd/ml) : Dissolve 0.108 g of palladium nitrate in 10 ml of nitric acid (1+1), and after bringing up to 500 ml using water, add water to 20 ml of this solution to bring up to 200 ml.

Procedure:

1) Place 15 ml each of pretreated sample (see note) into four 20 ml volumetric flasks, and add standard solution (0.01 µg Cd/ml) to three of them in increments in the range of 0.1~2 ml so that one flask contains no standard solution and the other three have increasing concentrations of standard solution added to the sample. After adding nitric acid (1+1) to each of the solutions so they all have the same concentration of acid, bring up to volume using water. (Note: If the pretreated sample contains more than 0.01 µg of Cd, decrease the sampling volume so that this becomes less than 0.01 µg.)
2) Place equal volumes of at least 100 µl of each sample prepared in step 1) into small volumetric flasks, and add equal volumes of the palladium nitrate (II) solution (10 µg Pd/ml) to each, and mix well for measurement.

**Measurement:**

Measurement wavelength: 228.8 nm

Calibration curve concentration range: 0.2~2 ng/ml

Tube: High-density graphite tube

Sample injection volume: 10 µl

Heating conditions:

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 15 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Pb**

**Reagents:**

1) Pb standard solution (0.2 µg Pb/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Palladium nitrate (II) solution (10 µg Pd/ml) : Preparation is as described for Cd reagent, item 2).

**Procedure:**

1) Place 15 ml each of pretreated sample (see note) into four 20 ml volumetric flasks, and add standard solution (0.2 µg Pb/ml) to three of them in increments in the range of 0.1~2 ml so that one flask contains no standard solution and the other three have increasing concentrations of standard solution added to the sample. After adding nitric acid (1+1) to each of the solutions so they all have the same concentration of acid, bring up to volume using water. (Note: If the pretreated sample contains more than 0.1 µg of Pb, decrease the sampling volume so that this becomes less than 0.1 µg.)
2) Place equal volumes of at least 100 µl of each sample prepared in step 1) into small volumetric flasks, and add equal volumes of the palladium nitrate (II) solution (10 µg Pd/ml) to each, and mix well for measurement..

**Measurement:**

Measurement wavelength: 283.3 nm

Calibration curve concentration range: 2~20 ng/ml

Tube: High-density graphite tube

Sample injection volume: 20 µl

Heating conditions:

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

### 10.1.3 Flame Atomic Absorption Method

**a) Target elements**

Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn

**b) Measurement procedure**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions. For preparation of the standard solutions for generating the calibration curve, refer to Cookbook Section 2, item 3 Preparing Standards.

- **Ca**

**Reagents**:

1) Ca standard solution (10 µg Ca/ml) :Refer to Cookbook Section 2, item 3 Preparing standards
2) La solution (50 g/l) : Dissolve 67 g of lanthanum chloride by adding small quantities of hydrochloric acid (1+1) little by little, and then add water up to a volume of 500 ml.

**Procedure:**

1) Place a suitable volume of pretreated sample (containing 5~150 µg of Ca) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then, after adding 3 ml of La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for correction of the value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 1~30 ml of the Ca standard into 50 ml volumetric flasks, add 3 ml of lanthanum solution (50 g/l) to each flask, and add water to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.3~6 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 9).

**Remarks:**

When Na is present in amounts greater that 200 times that of the Ca, and even the addition of La does not completely control the interference, conduct measurement using the $N_2O$-$C_2H_2$ flame (refer to Cookbook Section 3, item 6.4, 10).

- **Cd**

**Reagents:**

1) Cd standard solution (10 μg of Cd/ml) : refer to Cookbook Section 2, item 3 Preparing Standards.
2) Ammonium dihydrogen citrate (10 g/l): Dissolve 10 g of ammonium dihydrogen citrate in approximately 80 ml of water. Add 2~3 drops of m-Cresol Purple solution (1 g/l), and after adding enough drops of aqueous ammonia (1+1) to adjust the pH to about 9, add water to a volume of 100 ml. Transfer this to a separating funnel, add 2 ml of diethyl sodium dithiocarbamate solution (10 g/l) and 10 ml of butyl acetate. After vigorously vibrating the solution, set it aside. Separate off the ammonium dihydrogen citrate layer and pass it through dry filter paper to eliminate the minute butyl acetate bubbles.
3) m-Cresol Purple solution (1 g/l) : Dissolve 0.1 g of m-cresol purple in 50 ml of ethanol, and add water to volume of 100 ml.
4) diethyl sodium dithiocarbamate solution (10 g/l) : Dissolve 1.3 g of sodium dithiocarbamate in water, and bring volume to 100 ml.
5) Butyl acetate

**Procedure**:

1) Place a suitable amount of pretreated sample (containing 0.5~10 μg of Cd) in a separating funnel, and add 10 ml of ammonium dihydrogen citrate solution (10 g/l) and 2~3 drops of indicator m-Cresol Purple solution (1 g/l). Then add aqueous ammonia (1+1) until the solution becomes slightly purple.

   Then add 5 ml of diethyl sodium dithiocarbamate solution (10 g/l), and after shaking the solution, add 10 ml of butyl acetate and vigorously shake for about 1 minute before setting the solution down. Separate off the butyl acetate layer and place it in a 20 ml volumetric flask. Add 5 ml of butyl acetate to the remaining aqueous layer, and repeat the extraction procedure. Add this extracted butyl acetate layer to the previous volumetric flask. Keep adding butyl acetate until it is brought up to the 20 ml volume. This will be used in measurement.
2) For the calibration curve, prepare stepwise standard solutions over the calibration curve concentration range using the Cd standard solution (10 μg of Cd/ml), and use the same procedure as that for the sample.

**Measurement**:

Measurement wavelength: 228.8 nm

Calibration curve concentration range: 0.02~0.5 μg/ml (concentration after extraction)

Measurement conditions:

Lamp current value : 8 mA

Slit width : 0.5 nm

Lamp mode : BGC-$D_2$

Burner height : 7 mm

Support gas : Air

Fuel gas flow rate :

$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

- **Cu I** (When concentration is within the quantitation range of 0.2 ~ 4 μg/ml, and there are no interfering components)

**Reagents**:

Cu standard solution (10 μg of Cu/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The pretreated sample may be directly used for measurement, or it may be diluted with water so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.
2) For the calibration curve, place 2~40 ml of Cu standard solution (10 μg of Cu/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid repeat the extraction procedure. Add this extracted butyl ac. Add this extracted butyl acetate layer to the previous volumetric flask. Keep adding butyl acetate until it is brought up to the 20 ml volume. This will be used in measurement.

**Measurement**:

Measurement wavelength: 324.7 nm

Calibration curve concentration range: 0.2~4 μg/ml (concentration in solution after extraction)

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 15).

- **Cu II** (When Cu concentration is below the quantitation range)

**Reagents**:

1) Cu standard solution (10 μg of Cu/ml) : Same as for Cu I

2) Ammonium dihydrogen citrate (10 g/l)
3) m-Cresol Purple solution (1 g/l)
4) diethyl sodium dithiocarbamate solution (10 g/l) :
5) Butyl acetate

Items 2), 3), 4) and 5) are prepared as in 2) ~ 5), respectively, for the Cd reagents.

**Procedure**:

1) Place a suitable amount of pretreated sample (containing 2 ~ 40 μg of Cu) in a separating funnel, and proceed as described in step 1) of the Cd procedure.
2) For the calibration curve, prepare stepwise standard solutions over the calibration curve concentration range using the Cu standard solution (10 μg of Cd/ml). se the same procedure as that for the sample.

**Measurement**

Measurement wavelength: 324.7 nm

Calibration curve concentration range: 0.1~2 μg/ml (concentration in solution after extraction)

**Measurement conditions:**

Lamp current value : 6 mA
Slit width : 0.5 nm
Lamp mode : BGC-$D_2$
Burner height : 7 mm
Support gas : Air
Fuel gas flow rate :
$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

- **Fe**

**Reagents**:

Fe standard solution (10 μg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.
2) For the calibration curve, place 3~60 ml of Fe standard solution (10 μg of Fe/ml) in stepwise volumes in 100 ml volumetric flasks, and after adding acid using the same

conditions as that for the sample, bring up to volume with water.

**Measurement**

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.3~6 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16).

- **K**

**Reagents**:

K standard solution (10 μg of K/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.
2) For the calibration curve, place 1~10 ml of K standard solution (10 μg of K/ml) in stepwise volumes in 100 ml volumetric flasks, and after adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement**:

Measurement wavelength: 766.5 nm

Calibration curve concentration range: 0.1~1 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 19).

- **Mg**

**Reagents**:

1) Mg standard solution (5 μg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50g/l) : Same as item 2) for Ca reagent

**Procedure:**

1) Place a suitable volume of pretreated sample (containing .2~2.5 μg of Mg) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then add 3 ml of La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for correction of the value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of .5~5 ml of the Mg standard into 50 ml volumetric flasks, add 3 ml of lanthanum solution (50 g/l) to each flask, and add

water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 285.2 nm

Calibration curve concentration range: 0.05~0.5 µg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

- **Mn**

Reagents:

Mn standard solution (10 µg of Mn/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.
2) For the calibration curve, place 2~30 ml of Mn standard solution (10 µg of Mn/ml) in stepwise volumes in 100 ml volumetric flasks, and after adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement**:

Measurement wavelength: 279.5 nm

Calibration curve concentration range: 0.2~3 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 23).

- **Na**

**Reagents**:

Na standard solution (5 µg of Na/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.
2) For the calibration curve, place 1~10 ml of Na standard solution (5 µg of Na/ml) in stepwise volumes in 100 ml volumetric flasks, and after adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement**:

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 0.05~0.5 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 24).

- Pb

**Reagents**:

1) Pb standard solution (10 µg of Pb/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Ammonium dihydrogen citrate (10 g/l)
3) m-Cresol Purple solution (1 g/l)
4) diethyl sodium dithiocarbamate solution (10g/l) :
5) Butyl acetate

Items 2), 3), 4) and 5) are prepared as in 2) ~ 5), respectively, for the Cd reagents.

Procedure:

1) Place a suitable amount of pretreated sample (containing 6 ~ 60 µg of Pb) in a separating funnel, and proceed as described in step 1) of the Cd procedure.
2) For the calibration curve, prepare stepwise standard solutions of Pb standard solution, and use the same procedure as that for the sample.

**Measurement**:

Measurement wavelength: 217.0 nm

Calibration curve concentration range: 0.3~3 µg/ml (concentration in solution after extraction)

**Measurement conditions:**

Lamp current value : 12 mA

Slit width : 0.5 nm

Lamp mode : BGC-$D_2$

Burner height : 7 mm

Support gas : Air

Fuel gas flow rate :

$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

- **Zn I** (When concentration is within the quantitation range of 0.05 ~ 1 µg/ml, and there are no interfering components)

**Reagents:**

Zn standard solution (10 µg of Zn/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) The pretreated sample may be directly used for measurement, or it may be diluted with

hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for correction of the value obtained in sample measurement.

2) For the calibration curve, place .5~10 ml of Zn standard solution (10 μg of Zn/ml) in stepwise volumes in 100 ml volumetric flasks, and after adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement**:

Measurement wavelength: 213.9 nm
Calibration curve concentration range: 0.05~1 μg/ml
Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 44).

- **Zn II** (When Zn concentration is below the quantitation range)

Reagents:

1) Zn standard solution (10 μg of Zn/ml) : Same as for Zn I
2) Ammonium dihydrogen citrate (10 g/l)
3) m-Cresol Purple solution (1 g/l)
4) diethyl sodium dithiocarbamate solution (10 g/l) :
5) Butyl acetate

Items 2), 3), 4) and 5) are prepared as in 2) ~ 5), respectively, for the Cd reagents.

**Procedure**:

1) Place a suitable amount of pretreated sample (containing 0.5 ~ 10 μg of Zn) in a separating funnel, and proceed as described in step 1) of the Cd procedure.
2) For the calibration curve, prepare stepwise standard solutions over the calibration curve concentration range using the Zn standard solution (10 μg of Zn/ml), and use the same procedure as that for the sample.

**Measurement**:

Measurement wavelength: 213.9 nm
Calibration curve concentration range: 0.02~0.5 μg/ml (concentration in solution after extraction)
Measurement conditions:

Lamp current value : 8 mA
Slit width : 0.5 nm
Lamp mode : BGC-$D_2$
Burner height : 7 mm
Support gas : Air
Fuel gas flow rate :

$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

### 10.1.4 Hydride Vapor Generation Atomic Absorption Method

**a) Target element**

As

**b) Measurement Procedures**

**Reagents**:

1) As standard solution (1 μg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards.
2) Potassium iodide solution (200 g/l) : Dissolve 20 g of potassium iodide in water and bring to 100 ml volume.
3) Sodium tetrahydroborate solution (0.5 w/v%) : Dissolve 2.5g of sodium tetrahydroborate in 500 ml of sodium hydroxide solution (0.1 mol/l).
4) Hydrochloric acid

**Procedure:**

1) Add ml of hydrochloric acid (1+1) to 10 ml of pretreated sample, and 2 ml of potassium iodide solution, and then heat, without boiling. After allowing to cool, add 20 ml of water for measurement.
2) For the calibration curve, use the As standard solution (1 μg/ml) to prepare standard solutions of incremental concentrations between 10~100 ng, add 4 ml of hydrochloric acid (1+1) and 2 ml of potassium iodide solution, and perform the same measurement procedure as that for the sample.

**Measurement:**

Connect the HVG-1 Hydride Vapor Generator to the atomic absorption spectrophotometer, and measure the sample. For operation of the HVG-1, refer to the documentation accompanying the HVG-1.

Measurement wavelength: 193.7 nm

Calibration curve concentration range: 0.5~5.0 ng/ml

**Measurement conditions:**

Lamp current value: 14 mA

Slit width: 0.5 nm

Lamp mode: BGC-$D_2$

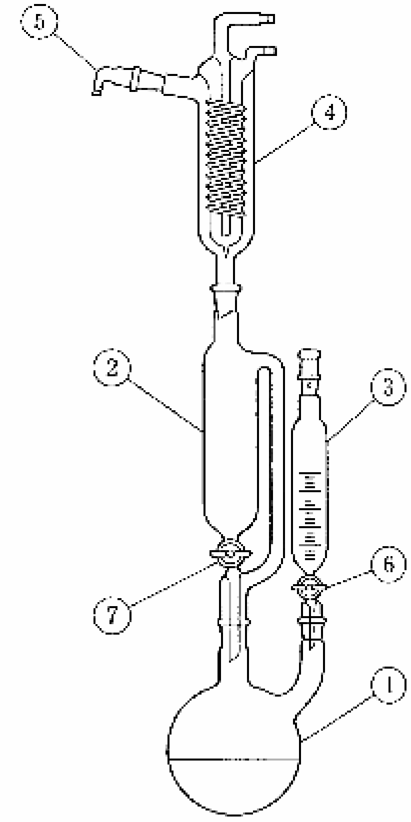
### 10.1.5 Reduction Vaporization Atomic Absorption Method

**a) Target element**

Total Hg

**b) Sample pretreatment**

Place 5~10 g of sample in a decomposition flask (example of a decomposition flask is illustrated in the following item), and wet with about 5 ml of water. To this flask, mount a fraction collector and above that a cooling circulator. Introduce 10~20 ml of nitric acid and 10 ml of sulfuric acid into the fraction collector (3), and then turn cock A to gradually introduce the contents to the decomposition flask. (If extreme amounts of bubbles are generated, it is advisable to let it sit overnight.) With cock B in the open position to allow condensation to circulate through the decomposition flask, gradually heat up the flask. Once the intense reaction is completed, close cock B and continue heating. Periodically open cock B to allow condensation to return from the fraction collector to the decomposition flask. Rinse the cooling circulator with a small amount of water, add 5~10 ml of urea solution (urea 200 g/l), boil for a short time, and after cooling to below 60°C, add 2 ml of potassium permanganate solution (potassium permanganate 50 g/l), and boil again. At this time, if the permanganic acid color disappears, repeat the addition of potassium permanganate solution until the color remains for at least 10 minutes. After allowing to cool, add hydrochloride hydroxyamine (10 w/v%), reduce the excess potassium permanganate, and add water to bring solution to 250 ml for measurement.



(1) 2-port round bottom flask
(2), (3) Cylindrical fraction funnels
(4) Friedlich cooler
(5) Bent tube
(6) Cock A

**c) Measurement procedure**

**Reagents:**

1) Hg standard solution (0.1 µg Hg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Stannous chloride solution (10 w/v%) : Add 10 g of stannous chloride to 60 ml of sulfuric acid (sulfuric acid to water ratio 1:20), and while heating, mix to dissolve. After cooling, bring up to 100 ml using water.

**Procedure:**

1) The pretreated sample may be measured as it is.

2) For the calibration curve, prepare standard solutions starting with incremental volumes between 2~12 ml of the Hg standard solution (0.1 µg Hg/ml), then adding 20 ml of sulfuric acid (1+1), and bringing up to 250 ml using water.

**Measurement:**

Connect the MVU-1A Mercury Vaporizer Unit to the atomic absorption spectrophotometer, and measure the sample. For details on operation of the MVU-1A, refer to its accompanying documentation.

Measurement wavelength: 253.7 nm
Calibration curve concentration range: 1~5 ng/ml
Measurement conditions:
  Lamp current: 4 mA
  Slit width: 0.5 nm
  Lamp mode: BGC-$D_2$

## 10.2 Grains, Beans, and Potatoes Analysis Method

Same as analysis method described in 10.1 Vegetables and Fruits Analysis Method

## 10.3 Meat, and Fish Analysis Method

Same as analysis method described in 10.1 Vegetables and Fruits Analysis Method

## 10.4 Fats, Oils, and Dairy Products Analysis Method

**Reference materials:**

Health Testing Methods Commentary, Japan Pharmaceutical Society Publication, Kanehara Publishing Co., Foodstuffs Analysis Methods, Japan Foodstuffs Manufacturing Society, Foodstuffs Analysis Methods Editorial Commission Publication (Korin Co.)

### 10.4.1 Sample Pretreatment

**a) Nitric acid, perchloric acid decomposition**

This is the same as the nitric acid, perchloric acid decomposition of item 10.1.1 a), however, perchloric acid and the sample often do not mix, preventing successful decomposition. In such cases, use the procedure described in b) Ashing by drying.

**b) Ashing by drying**

Place 5~10 g of sample in a quartz beaker, add 1~3 ml of sulfuric acid, and gently heat on a hot plate at 120°C. After the components, which are volatilized at low temperatures are driven off, continue heating the sample until carbonization occurs. (At this time, if intense bubbling in the sample occurs, add 0.5 ml of nitric acid.) Place this in an electric furnace, increase heat at a rate of 100°C per hour, and at about 500°C perform ashing over a period of several hours. If ashing is incomplete, wet with 2~5 ml of 50% magnesium nitrate solution or nitric acid (1+1). After drying, continue ashing. Add 2~4 ml of water to the ash, and after drying, add 5 ml of hydrochloric acid to dissolve the salts. Use water to prepare fixed volumes of the measurement solution.

**Remarks:**

There is a possibility of volatilizing most of the elements, with Cd being volatilized during ashing above 500°C. If halogens are coexistent, As, Sb, Sn Zn, etc. will be volatilized. Heating above 550°C will greatly reduce the element collection rate.

### 10.4.2 Electrical Heating Atomic Absorption Method

**a) Target elements**

Cd, Pb, Cu, Fe, Zn

**b) Measurement procedure**

Measurement is conducted using the following procedure. The lamp current value, and the slit width used are in accordance with Cookbook Section 4, item 7.5.

- **Cd**

Reagents:

Same as those described in item 10.1.2 Electrical Heating Atomic Absorption Method, Cd.

Procedure:

Using 15 ml pretreated sample volumes, follow the procedure described in item 10.1.2 Electrical Heating Atomic Absorption Method, Cd.

Measurement:

Same as described in item 10.1.2 Electrical Heating Atomic Absorption Method, Cd.

- **Pb**

Reagents:

Same as those described in item 10.1.2 Electrical Heating Atomic Absorption Method, Pb.

Procedure:

Using 15 ml pretreated sample volumes, follow the procedure described in item 10.1.2 Electrical Heating Atomic Absorption Method, Pb.

Measurement:

Same as described in item 10.1.2 Electrical Heating Atomic Absorption Method, Pb.

- **Cu** (direct quantitation of oil)

Reagents:

Cu standard solution (0.2 μg Cu/ml): Prepare a 10 mg Cu/ml aqueous solution referring to Cookbook Section 2, item 3 Preparing Standards. Introduce 1 ml of this solution into a 50 ml volumetric flask, add 10 ml of methyl alcohol and mix well. Then bring up to volume using 4-methyl-2-pentanone (MIBK), for the Cu standard solution (0.2 μg Cu/ml). Or, measure out 63.257 mg of the oily metallic standard reagent copper cyclohexylbutyric acid (molecular weight 402.04), add 3 ml of xylene and 5 ml of 2-ethylhexanoic acid. Gently heat to dissolve until it is clear. After cooling to room temperature, transfer the solution to a 100 ml volumetric flask and bring up to volume using MIBK (100 μg Cu/ml). Next, transfer 4 ml of this solution to a 100 ml volumetric flask and bring up to volume using MIBK (4 μg Cu/ml), and then transfer 5 ml of this solution to a 100 ml volumetric flask and bring up to volume using MIBK for the final Cu standard solution (0.2 μg Cu/ml).

Procedure:

1) Using a suitable amount of sample, dilute with MIBK so that the concentration is within the quantitation range (dilution factor of 5) for measurement.
2) For the calibration curve, introduce 0.5~5 ml of Cu standard solution (0.2 μg Cu/ml) in incremental volumes into 50 ml volumetric flasks, and bring all the solutions up to volume using MIBK.

Measurement:

Measurement wavelength: 324.7 nm

Calibration curve concentration range: 1~20 ng/ml

Tube: pyrolytic graphite tube

Sample injection volume: 10 μl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 80 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 750 | 15 | R | 1.0 |
| 4 | 750 | 15 | S | 1.0 |
| 5 | 750 | 3 | S | 0.0H |
| 6 | 2400 | 4 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- **Fe** (direct quantitation of oil)

  Reagents:

  Fe standard solution : (0.5 µg Fe/ml): Prepare a 10 mg Fe/ml aqueous solution referring to Cookbook Section 2, item 3 Preparing Standards. Introduce 2.5 ml of this solution into a 50 ml volumetric flask. Add 10 ml of methyl alcohol and mix well. Then bring up to volume using 4-methyl-2-pentanone (MIBK), for the Fe standard solution (0.5 µg Fe/ml).

  Or measure out 60.023 mg of the oily metallic standard reagent ferrous cyclohexylbutyric acid (molecular weight 670.45). Add 3 ml of xylene and 5 ml of 2-ethylhexanoic acid. Gently heat to dissolve until it is clear, and after cooling to room temperature, transfers the solution to a 100 ml volumetric flask. Then bring up to volume using MIBK (100 µg Fe/ml). Next, transfer 5 ml of this solution to a 100 ml volumetric flask and bring up to volume using MIBK (5 µg Fe/ml), and then transfer 10 ml of this solution to a 100 ml volumetric flask. Then bring up to volume using MIBK for the final Fe standard solution (0.5 µg Fe/ml).

  Procedure:

  1) Using a suitable amount of sample, dilute with MIBK so that the concentration is within the quantitation range (dilution factor of 5) for measurement.
  2) For the calibration curve, introduce 0.5~5 ml of Fe standard solution (0.5 µg Fe/ml) in incremental volumes into 50 ml volumetric flasks, and bring all the solutions up to volume using MIBK.

  Measurement:

  Measurement wavelength: 248.3 nm

  Calibration curve concentration range: 5~50 ng/ml

  Tube: pyrolytic graphite tube

  Sample injection volume: 10 µl

  Heating conditions:

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 80 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 750 | 15 | R | 1.0 |
| 4 | 750 | 15 | S | 1.0 |
| 5 | 750 | 3 | S | 0.0H |
| 6 | 2400 | 4 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- **Zn** (direct quantitation of oil)

  Reagents:

Zn standard solution : (0.1 µg Zn/ml): Prepare a 5 mg Zn/ml aqueous solution referring to Cookbook Section 2, item 3 Preparing Standards. Introduce 1 ml of this solution into a 50 ml volumetric flask, add 10 ml of methyl alcohol and mix well. Then bring up to volume using 4-methyl-2-pentanone (MIBK), for the Zn standard solution (0.1 µg Zn/ml).

Or, measure out 61.781 mg of the oily metallic standard reagent zinc cyclohexylbutyric acid (molecular weight 403.86). Add 3 ml of xylene and 5 ml of 2-ethylhexanoic acid. Gently heat to dissolve until it is clear, and after cooling to room temperature, transfer the solution to a 100 ml volumetric flask and bring up to volume using MIBK (100 µg Zn/ml). Next, transfer 2 ml of this solution to a 100 ml volumetric flask and bring up to volume using MIBK (2 µg Zn/ml). Then transfer 5 ml of this solution to a 100 ml volumetric flask and bring up to volume using MIBK for the final Zn standard solution (0.1 µg Zn/ml).

Procedure:

1) Using a suitable amount of sample, dilute with MIBK so that the concentration is within the quantitation range (dilution factor of 5) for measurement.
2) For the calibration curve, introduce 0.5~5 ml of Zn standard solution (0.1 µg Zn/ml) in incremental volumes into 50 ml volumetric flasks, and bring all the solutions up to volume using MIBK.

Measurement:

Measurement wavelength: 213.9 nm

Calibration curve concentration range: 1~10 ng/ml

Tube: High-density graphite tube

Sample injection volume: 10 µl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 80 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 300 | 15 | R | 1.0 |
| 4 | 300 | 20 | S | 1.0 |
| 5 | 300 | 3 | S | 0.0 |
| 6 | 1300 | 3 | S | 0.0 |
| 7 | 2600 | 2 | S | 0.1 |

### 10.4.3 Flame Atomic Absorption Method

a) Target elements

Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn

b) Measurement procedure

Using the pretreated samples described in Item 10.4.1, use the same procedure as described in item 10.1.3 Flame Atomic Absorption Method

### 10.4.4 Hydride Vapor Generation Atomic Absorption Method

a) Target elements

As

b) Measurement procedure

Use the same procedure as described in item 10.1.4 Hydride Vapor Generation Atomic Absorption Method, b) Measurement procedure.

### 10.4.5 Reduction Vaporization Atomic Absorption Method

a) Target elements

Total Hg

b) Sample pretreatment

Use the same procedure described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, b) Sample pretreatment.

c) Measurement procedure

Use the same procedure as described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, c) Measurement procedure.

## 10.5 Spirits, Alcoholic Beverage Analysis

Reference materials:

Health Testing Methods Commentary, Japan Pharmaceutical Society Publication, Kanehara Publishing Co.,

Foodstuffs Analysis Methods, Japan Foodstuffs Manufacturing Society, Foodstuffs Analysis Methods Editorial Commission Publication (Korin Co.)

### 10.5.1 Sample Pretreatment

a) Nitric acid, perchloric acid decomposition

Introduce 10~20 g of sample into a conical beaker. Add 25 ml of nitric acid, and then follow the same procedure as that described in item 10.1.1 Sample Pretreatment, a) Nitric acid, perchloric acid decomposition.

Remark:

When a large part of the sample is sugar, a large amount of acid must be used and there is a possibility of contamination of the target element with reagent. In this case, either decrease the sample amount or use the ashing by drying procedure described next.

b) Ashing by drying

Dissolve 10~20 g of sample in water, and after drying through vaporization, continue heating until partial carbonization occurs. Place this in an electric furnace, and follow the procedure described in item 10.1.1 Sample Pretreatment, b) Ashing by drying.

c) Hydrochloric acid extraction

Add hydrochloric acid (1+1) to 10~20 g of sample at a ratio of 2 ml/10 g of sample. Set aside for 1 hour, periodically shaking the flask to mix the contents. Then, either filter and use the filtrate for measurement, or centrifuge at 4,000 rpm for 5 minutes and use the supernatant for measurement.

**Remark:**

Used for measurement of K, Na, Mg, Cu, Mn, Zn.

### 10.5.2 Electrical Heating Atomic Absorption Method

a) Target elements

Cd, Cr, Cu, Fe, Mn, Pb, Sn, Zn

b) Measurement procedure

Measurement is conducted using the following procedure. The lamp current and slit width is as described in Cookbook Section 4, item 7.5 Element Specific Conditions.

- **Cd**

Reagents:

Same as that described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Cd.

Procedure:

Using 15 ml aliquots of sample pretreated according to a) or b), follow the same procedure as described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Cd.

Measurement:

Same as that described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Cd.

- Cr

Reagents:

Cr standard solution (0.01 µg Cr/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Samples pretreated using method a) or b) (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. At this time, perform the same pretreatment on a suitable volume of water, and conduct measurement

on this solution. The value obtained may be used to correct the value obtained in actual sample measurement.

2) For the calibration curve, introduce 2~10 ml of Cr standard solution (0.01 µg Cr/ml) in incremental volumes into 20 ml volumetric flasks. Add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 357.9 nm

Calibration curve concentration range: 1~5 ng/ml

Tube: Pyrolytic graphite tube

Sample injection volume: 10 µl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 20 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2400 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Cu**

Reagents:

Cu standard solution (0.01 µg Cu/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Samples pretreated using method a) or b) (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. At this time, perform the same pretreatment on a suitable volume of water, and conduct measurement on this solution. The value obtained may be used to correct the value obtained in actual

sample measurement.

2) For the calibration curve, introduce 2~10 ml of Cu standard solution (0.01 µg Cu/ml) in incremental volumes into 20 ml volumetric flasks. Add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 324.7 nm
Calibration curve concentration range: 1~5 ng/ml
Tube: Pyrolytic graphite tube
Sample injection volume: 20 µl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 20 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Fe**

Reagents:

Fe standard solution (0.02 µg Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Samples pretreated using method a) or b) (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. At this time, perform the same pretreatment on a suitable volume of water, and conduct measurement

on this solution. The value obtained may be used to correct the value obtained in actual sample measurement.

2) For the calibration curve, introduce 2~10 ml of Fe standard solution (0.02 μg Fe/ml) in incremental volumes into 20 ml volumetric flasks. Add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 248.3 nm
Calibration curve concentration range: 2~10 ng/ml
Tube: Pyrolytic graphite tube
Sample injection volume: 20 μl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 20 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Mn**

Reagents:

Mn standard solution (0.01 μg Mn /ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Samples pretreated using method a) or b) (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. At this time, perform the same pretreatment on a suitable volume of water, and conduct measurement

on this solution. The value obtained may be used to correct the value obtained in actual sample measurement.

2) For the calibration curve, introduce 0.5~4 ml of Mn standard solution (0.01 μg Mn/ml) in incremental volumes into 20 ml volumetric flasks. Add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 379.5 nm

Calibration curve concentration range: 0.2~2 ng/ml

Tube: Pyrolytic graphite tube

Sample injection volume: 20 μl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 20 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Pb**

Reagents:

Same as that described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Pb.

Procedure:

Using 15 ml aliquots of sample pretreated according to a) or b), follow the same procedure as described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Pb.

Measurement:

Same as that described in item 10.1.2 Electrical Heating Atomic Absorption Method, for Pb.

- **Sn**

Reagents:

1) Sn standard solution (0.2 μg Sn /ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Palladium nitrate (II) solution (100 μg Pd/ml) : Add 10 ml of nitric acid (1+1) to 0.108

g of palladium nitrate (II) to dissolve, and bring up to 500 ml using water.

Procedure:

1) Samples pretreated using method b) (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. In either case, add the palladium nitrate (II) solution so that its concentration becomes 10 µg/ml. At this time, perform the same pretreatment on a suitable volume of water, and conduct measurement on this solution. The value obtained may be used to correct the value obtained in actual sample measurement.
2) For the calibration curve, introduce 1~10 ml of Sn standard solution (0.2 µg Sn/ml) in incremental volumes into 20 ml volumetric flasks. Add 2 ml of palladium nitrate (II) solution (100 µg Pd/ml), and add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 386.3 nm

Calibration curve concentration range: 10~100 ng/ml

Tube: Pyrolytic graphite tube

Sample injection volume: 20 µl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 20 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 800 | 10 | R | 1.0 |
| 4 | 800 | 20 | S | 1.0 |
| 5 | 800 | 3 | S | 0.0H |
| 6 | 2400 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

- **Zn**

Reagents:

Zn standard solution (0.01 µg Zn /ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Pretreated samples (samples without cloudiness, and those with low viscosity may be measured without pretreatment) may be used directly or diluted with nitric acid (1+100) so that the concentration is within the quantitation range. At this time, perform the same

pretreatment on a suitable volume of water, and conduct measurement on this solution. The value obtained may be used to correct the value obtained in actual sample measurement.

2) For the calibration curve, introduce 2~10 ml of Zn standard solution (0.01 µg Zn/ml) in incremental volumes into 20 ml volumetric flasks, add acid according to the same conditions used for the sample, and add water to bring all the solutions up to volume.

Measurement:

Measurement wavelength: 213.9 nm

Calibration curve concentration range: 1~5 ng/ml

Tube: High-density graphite tube

Sample injection volume: 10 µl

Heating conditions:

| | TEMP (°C) | TIME (sec) | HEAT | GAS (l/min) |
|---|---|---|---|---|
| Stage 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 450 | 10 | R | 1.0 |
| 4 | 450 | 20 | S | 1.0 |
| 5 | 450 | 3 | S | 0.0 |
| 6 | 1800 | 3 | S | 0.0 |
| 7 | 2400 | 3 | S | 1.0 |

### 10.5.3 Flame Atomic Absorption Method

a) Target elements

Ca, Cd, Cu, Ge, K, Mg, Mn, Na, Pb, Zn

b) Measurement procedure

Using samples pretreated according to item 10.5.1, the procedure is the same as that described in item 10.1.3 Flame Atomic Absorption Method.

### 10.5.4 Hydride Vapor Generation Atomic Absorption Method

a) Target elements

As

b) Measurement procedure

Same as procedure described in item 10.1.4 Hydride Vapor Generation Atomic Absorption Method, b) Measurement procedure

### 10.5.5 Reduction Vaporization Atomic Absorption Method

a) Target elements

Hg

b) Sample pretreatment

Same as that described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, b) Sample pretreatment

c) Measurement procedure

Same as that described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, c) Measurement procedure

## 10.6 Processed Foods Analysis Method

Reference materials:

Health Testing Methods Commentary, Japan Pharmaceutical Society Publication, Kanehara Publishing Co.,

Foodstuffs Analysis Methods, Japan Foodstuffs Manufacturing Society, Foodstuffs Analysis Methods Editorial Commission Publication (Korin Co.)

### 10.6.1 Sample Pretreatment

Same as item 10.1.1 Sample Pretreatment

### 10.6.2 Electrical Heating Atomic Absorption Method

**a) Target elements**

Cd, Cr, Cu, Fe, Mn, Pb, Sn, Zn

**b) Measurement procedure**

Using pretreated samples, follow the procedure described in item 10.5.2 Electrical Heating Atomic Absorption Method

### 10.6.3 Flame Atomic Absorption Method

**a) Target elements**

Ca, Cd, Cu, Fe, Mg, Mn, Na, Pb, Zn

**b) Measurement procedure**

Using pretreated samples, follow the procedure described in item 10.1.3 Flame Atomic Absorption Method.

### 10.6.4 Hydride Vapor Generation Atomic Absorption Method

**a) Target elements**

As

**b) Measurement procedure**

Follow the procedure described in item 10.1.4 Hydride Vapor Generation Atomic Absorption Method, b) Measurement procedure.

### 10.6.5 Reduction Vaporization Atomic Absorption Method

**a) Target elements**

Total Hg

**b) Sample pretreatment**

Follow the same procedure described in 10.1.5 Reduction Vaporization Atomic Absorption

Method, b) Sample pretreatment

**c) Measurement procedure**

Follow the procedure described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, c) Measurement procedure.

# 11. Fertilizer and Feed Analysis

## 11.1 Fertilizer Analysis Method

**Reference materials:**

Fertilizer Analysis, Agriculture and Forestry Ministry Agricultural Technology Research Institute

### 11.1.1 Sample Pretreatment

**a) Total analysis**

- **Ca, Cd, Co, Cu, Fe, Mg, Mo, Ni, Pb, Zn (inorganic fertilizer)**

Place 2~5 g of sample in a tall beaker. Add 30 ml of hydrochloric acid and 10 ml of nitric acid. Cover with a watch glass, boil on a sand bath for 30 minutes, and boil over a water bath unydrrochloric acid and 10 ml of nitric acid. Cover with a watch glass, boil on a sand bath for 30 minutes, and boil over a water bath until dry. Add a little more nitric acid and boil until dry once again. After allowing to cool, add about 40 ml of hydrochloric acid (1+20), heat to dissolve. After cooling, add water to accurately bring up to 200 ml. Immediately filter through dry filter paper, and use the filtrate for measurement.

- **Ca, K, Mg (organic fertilizer, or fertilizer containing organic material)**

Place 5~10 g of sample in a platinum dish, ash at about 500°C then transfer to a tall beaker. Add 10 ml of hydrochloric acid and water to bring up to 30 ml. Boil for about 30 minutes, and after cooling, add water to accurately bring volume to 250 ml. Then filter through dry filter paper, and use the filtrate for measurement.

- **K (potassium salt)**

Place 2.5 g of sample in a 300 ml tall beaker. Add 200 ml of water and a small amount of hydrochloric acid to acidify. Cover with a watch glass and boil for about 15 minutes to dissolve. After cooling, add water to accurately bring volume up to 250 ml. Then filter through dry filter paper, and use the filtrate for measurement.

- **K (vegetation ash)**

Place 5 g of sample in a tall beaker. Wet with a small amount of water, cover with a watch glass, add 10 ml of hydrochloric acid and water, and boil for about 30 minutes. Next, boil until dry and after performing silicic acid separation,, add water to accurately bring volume to 500 ml. Then filter through dry filter paper and use the filtrate for measurement.

- **K (complex fertilizer)**

Place 5 g of sample in a 300 ml tall beaker (for samples containing organic material, place in platinum dish beforehand, and ash at about 500°C), add 10 ml of hydrochloric acid and bring up to 30 ml with water. Then boil for about 10 minutes. Next, add 150 ml of water, boil, and after cooling, add water to accurately bring volume to 500 ml. Then filter through dry filter paper and use the filtrate for measurement.

- **K (potassium ore)**

  1)Place 1 g of sample in a platinum dish, and add several drops of water to wet. 2)Add 5 ml of 46% hydrofluoric acid and 0.5 ml of perchloric acid, and heat on a hot plate until white fumes of perchloric acid are generated. 3)After allowing to cool, , add 5 ml of 46% hydrofluoric acid, partially cover with a poly-4-fluoroethylene watch glass, and heat on a hot plate until almost dry. 4)After allowing to cool, add 5 ml of hydrochloric acid (1+1) and a small amount of water, and heat on a hot plate to dissolve. At this time, if dissolution is not complete due to incomplete decomposition, go back to step 2) and repeat the process to completely dissolve. After allowing to cool, transfer to a 100 ml volumetric flask, and add water to bring solution up to volume.

b) Water-soluble component analysis

- **Cd**

  Place 50 g of sample in a sample vial having a stopper. Add 10 times that amount of water (20°C), and shake in an oscillating mixer (200 oscillations per minute, oscillating width 4~5 cm) for 6 hours, and immediately filter through glass fiber filter paper having 1 μm pores. If filtering is noticeably difficult to perform, then centrifuge the previously mixed liquid at 3,000 rpm for 20 minutes, and use the supernatant for measurement.

- **Cu, Fe, Mn, Mo, Zn**

  Place 5 g of sample in a 500 ml volumetric flask, and add approximately 400 ml of water. Shake in an oscillating mixer at 30~40 rotations per minute for 30 minutes. Then bring up to volume with water, and immediately pass through dry filter paper. Use the filtrate for measurement.

- **Mg**

  Place 1 g of sample in a 500 ml triangular flask and add approximately 400 ml of water. Using a cooling circulator, boil for 30 minutes, and after allowing to cool, add water to accurately bring volume to 500 ml. Immediately pass through dry filter paper, and use the filtrate for measurement.

- **K (potassium salts)**

  Place 2.5 g of sample in a 300 ml tall beaker. Add about 200 ml of water, and boil for 15 minutes. After cooling, add water to accurately bring volume up to 250 ml. Then pass through dry filter paper, and use the filtrate for measurement.

- **K (complex fertilizer)**

  Place 5 g of sample in a small mortar, and add a small amount of water and grind well. Transfer the supernatant liquid into a 500 ml volumetric flask. After repeating this procedure 3 more times, transfer all of the remaining material in the mortar to the flask. Add water to bring up to approximately 400 ml, and shake at 30~40 rotations per minute in a rotating mixer for 30 minutes. Then bring up to volume with water. Pass through dry filter paper, and use the filtrate for measurement.

c) Soluble component analysis

- **Ca, Mg**

Place 2.5 g of sample in a tall beaker, and add 200 ml of 0.5 mol hydrochloric acid. Cover with a watch glass, and boil for 5 minutes. After cooling, add water to bring volume to 250 ml. Then pass through dry filter paper and use the filtrate for measurement.

**d) Citric acid soluble component analysis**

- **K, Mg, Mn**

Place 1 g of sample in a 250 ml volumetric flask. Add 150 ml of citric acid (citric acid 20 g/l) at 30°C, and shake at 30~40 rotations per minute in a rotating mixer for one hour (while maintaining 30°C during extraction). Quickly return to ambient temperature, and add water to bring up to volume. Quickly pass through dry filter paper. Use the filtrate for measurement.

### 11.1.2 Flame Atomic Absorption Method

a) Target elements

Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Zn

b) Measurement procedure

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions. For preparation of the standard solutions for generating the calibration curve, refer to Cookbook Section 2, item 3 Preparing Standards.

- **Ca**

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Ca.

- **Cd I** (When concentration is within the quantitation range of 0.05~ 1 μg/ml, and there are no interfering components)

**Reagents:**

Cd standard solution (10 μg of Cd/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for

correction of the value obtained in sample measurement.

2) For the calibration curve, place 0.5~10 ml of Cd standard solution (10 μg of Cd/ml) in incremental volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement:**

Measurement wavelength: 228.8 nm

Calibration curve concentration range: 0.05~1 mg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 11)

- **Cd II** (When Cd concentration is below the quantitation range, or when interfering components are present)

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Cd.

- **Co**

**Reagents:**

1) Co standard solution (10 μg of Co/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Cupferron solution (50 g/l) : Dissolve 5 g of cupferron (N-nitrosophenylhydroxylamine ammonium salt) in water and bring up to 100 ml.

3) Ammonium citrate solution (500 g/l) : Gradually add 250 ml of aqueous ammonia to 250 g of citric acid. While cooling to dissolve, add water to bring up to 500 ml.

**Remark:**

When there is a possibility that the ammonium citrate is contaminated with Co after dissolving with aqueous ammonia, adjust to pH 9 using aqueous ammonia and dilute nitric acid. Transfer this to a separating funnel. Add 25 ml of cupferron solution (50 g/l) and 25 ml of 4-methyl-2-pentanone (MIBK). After vigorously shaking to mix, set solution aside, discard the organic layer, and add water to the aqueous phase to bring up to 500 ml.

4) 4-methyl-2-pentanone (MIBK)

**Procedure:**

1) Place an appropriate amount of pretreated sample (containing 2.5~15 μg of Co) in a beaker. Add 5 ml of ammonium citrate, and adjust to pH 6~7 using nitric acid and aqueous ammonia. Transfer this liquid to a separating funnel, and add 10 ml of cupferron solution (50 g/l) and bring up to 50 ml using water. After accurately adding 5 ml of MIBK, shake vigorously for several minutes to mix, and then let stand. The organic phase is used for measurement.

2) For the calibration curve, prepare incremental standard solutions over the calibration curve concentration range using the Co standard solution (10 μg of Co/ml), and use the

same procedure as that for the sample.

**Measurement:**

Measurement wavelength: 240.7 nm

Calibration curve concentration range: 0.5~3 mg/ml (concentration after extraction)

**Measurement conditions:**

Lamp current value : 12 mA

Slit width : 0.2 nm

Lamp mode : BGC-$D_2$

Burner height : 7 mm

Support gas : Air

Fuel gas flow rate :

$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

- **Cu**

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Cu I.

- Fe

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Fe.

- K

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, K. Since this result expresses the amount of K, multiply by 1.205 to express amount of K2O.

- Mg

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Mg. Since this result expresses the amount of Mg, multiply by 1.658 to express amount of MgO.

- Mn

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Mn.

- Mo

**Reagents:**

1) Mo standard solution (10 μg of Mo/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) 8-quinolinol solution (200 g/l) : Place 20 g of 8-quinolinol (oxine) in a beaker, and heat

on a water bath. Add water to bring volume up to 100 ml.

3) 4-methyl-2-pentanone (MIBK)

**Procedure:**

1) Place an appropriate amount of sample (containing 25~300 μg of Mo) in a 100 ml volumetric flask. Add 10 ml of 1 mol hydrochloric acid, 5 ml of 8-quinolinol solution (200 g/l), and water to bring volume to about 80 ml. Shake vigorously to mix and then let stand. Accurately add 5 ml of MIBK, shake vigorously for 1~2 minutes and then let stand. Use the organic phase for measurement.
2) For the calibration curve, prepare incremental standard solutions of Mo standard solution over the quantitation range, and use the same procedure as that for the sample.

**Measurement:**

Measurement wavelength: 313.3 nm

Calibration curve concentration range: 5~30 μg/ml (concentration after extraction)

Measurement conditions:

Lamp current value : 12 mA

Slit width : 0.5 nm

Lamp mode : BGC-$D_2$

Burner height : 17 mm

Support gas : $N_2O$

Fuel gas flow rate : $C_2H_2$ 6.5 l/min

- **Ni**

**Reagents:**

1) Ni standard solution (10 μg of Ni /ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Ammonium nitrate solution (10 g/l)
3) m-Cresol Purple solution (1 g/l) : Dissolve 0.1 g of m-cresylic purple in 50 ml of ethanol, and add water to volume of 100 ml.
4) diethyl sodium dithiocarbamate solution (10 g/l) : Dissolve 1.3 g of sodium dithiocarbamate in water, and bring volume to 100 ml.
5) Butyl acetate

Items 2), 3), 4) and 5) are prepared as in 2) ~ 5), respectively, for the Cd reagents in item 10.1.3 Flame. Atomic Absorption Analysis Method

**Procedure:**

1) Place a suitable amount of pretreated sample (containing 5 ~ 30 μg of Ni) in a separating funnel, and proceed as described in step 1) of the Cd procedure in item 10.1.3

Flame. Atomic Absorption Analysis Method.

2) For the calibration curve, prepare incremental standard solutions of Ni standard solution over the calibration curve quantitation range, and use the same procedure as that for the sample.

**Measurement:**

Measurement wavelength: 232.0 nm

Calibration curve concentration range: 0.5~3 μg/ml (concentration after extraction)

Measurement conditions:

Lamp current value : 12 mA

Slit width : 0.2 nm

Lamp mode : BGC-$D_2$

Burner height : 7 mm

Support gas : Air

Fuel gas flow rate :

$C_2H_2$ 0.8 l/min (If the flame turns reddish when the sample is sprayed, decrease the amount of sample drawn up.)

- **Pb**

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Pb.

- **Zn I** (when Zn concentration is within the quantitation range of 0.05~1 μg/ml, and there are no interfering components)

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Zn I.

- **Zn II** (when the Zn concentration is below the quantitation range)

The analysis method is the same as that described in item 10.1.3 Flame Atomic Absorption Method, Zn II.

### 11.1.3 Hydride Vapor Generation Atomic Absorption Method

**a) Target elements**

As, Se

**b) Sample pretreatment**

- **Total As (fertilizer)**

Place 1~5 g of sample in a beaker. Wet with water, add 2 ml of sulfuric acid, about 5 ml of nitric acid, and 20 ml of perchloric acid. Heat until white fumes of perchloric acid are generated, and further, until the sample becomes concentrated almost to dryness. After cooling, add water to dissolve and after cooling, transfer to a 100 ml volumetric flask. Add water to bring up to volume, and pass through dry filter paper. Use the filtrate for measurement.

- **Water soluble As**

  The procedure is the same as that described in item 11.1.1 Sample Pretreatment, b) Water-soluble component analysis, Cd.

- **Total Se (inorganic fertilizer and rock phosphate)**

  Place 1~5 g of sample in a tall beaker. Wet with a small amount of water, and add 20 ml of nitric acid. Cover with a watch glass and gradually heat to decompose. When the liquid volume becomes about 5 ml, add about 10 ml more of nitric acid and heat again to completely decompose. Continue heating until the sample is nearly dry. Add approximately 20 ml of water and heat to dissolve. After allowing to cool, transfer to a 100 ml volumetric flask. Add 10 ml of hydrochloric acid, and add water to bring up to volume. Then pass through dry filter paper. Use the filtrate for measurement.

- **Total Se (sample containing organic material)**

  Place the sample in a Kjeldahl flask. Add 1~2 glass beads, and add approximately 10 ml of nitric acid for each 1g of sample. Attach an air cooling tube and gradually heat. Continue heating so that as the temperature gradually rises, the nitric acid begins to condense at the bottom of the cooling tube, and then heat for 10 minutes more. After cooling, carefully add 2~4 ml of perchloric acid. Attach the cooling tube and gradually heat for 15 minutes. Detach the cooling tube, heat again until the white fumes of perchloric acid are generated. Then continue heating for 15 minutes longer. Rinse the insides of the flask with a small amount of water, and heat again until the white fumes of perchloric acid are generated, and then allow to cool. Add approximately 20 ml of water to dissolve, and transfer to a 100 ml volumetric flask. Add 10 ml of hydrochloric acid , and add water to bring up to volume. Pass through dry filter paper, and use the filtrate for measurement.

c) Measurement procedure

- **As**

  Same procedure as that described in item 10.1.4 Hydride Vapor Generation Atomic Absorption Method, b) Measurement procedure

- **Se**

  **Reagents:**

  1) Se standard solution (1 μg of Se/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
  2) Sodium tetrahydroborate solution : Same procedure as that described in item 10.1.4 Hydride Vapor Generation Atomic Absorption Method, b) Measurement procedure, Reagents, 3).

  **Procedure:**

  1) The pretreated sample may be used for measurement as it is.
  2) For the calibration curve, prepare incremental standard solutions from the Se standard

solution (1 μg of Se/ml) with concentrations of Se ranging from 20~100 ng. Add 4 ml of hydrochloric acid (1+1), and then add water to bring all solutions up to a volume of 20 ml.

**Measurement:**

Measurement wavelength: 196.0 nm

Calibration curve concentration range: 1~5 ng/ml

Measurement conditions:

Lamp current value : 23 mA

Slit width : 0.5 nm

Lamp mode : BGC-$D_2$

### 11.1.4 Reduction Vaporization Atomic Absorption Method

**a) Target element**

Total Hg

**b) Sample pretreatment**

- **Fertilizer:**

Place a fixed amount of sample (2~5 g of inorganic fertilizer, or 5~10 g of fertilizer containing organic material) in a decomposition flask, and use the same procedure as that described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, b) Sample pretreatment , Procedure.

- **Rock phosphate**

Place 2 g of sample in a decomposition flask, and wet with a small amount of water. Add 25 ml of phosphoric acid (1+1) and 2~3 ml of potassium permanganate (potassium permanganate 50 g/l). Attach a cooling circulator and heat for about 1 hour to decompose. During this time, if the potassium permanganate color disappears, cool to below 60°C, and add 2~3 drop of potassium permanganate solution. Then heat. Repeat this procedure until the potassium permanganate color remains, and then heat for 10 minutes longer. After cooling, transfer to a 250 ml volumetric flask. Bring up to volume with water, and use this solution for measurement.

- **Water soluble Hg**

Same as that described in item 11.1.1 Sample Pretreatment, B) Water soluble Components, Cd

**c) Measurement procedure**

Same as that described in item 10.1.5 Reduction Vaporization Atomic Absorption Method, C) Measurement procedure.

## 11.2 Feed Analysis Method

### 11.2.1 Sample Pretreatment

Same as that described in item 10.1.1 Sample Pretreatment

### 11.2.2 Flame Atomic Absorption Method

**a) Target Elements**

Ca, Cd, Fe, Mg, Mn, Pb, Zn

**b) Measurement Procedure**

Measurement is conducted using the following procedure. The lamp current, slit width and flame conditions are as described in Cookbook Section 3, item 6.4 Element Specific Conditions. For preparation of standards for the calibration curves, refer to Cookbook Section 2, item 3 Preparing Standards.

- **Ca**

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Ca
- Cd

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Cd
- Cu I (when Cu concentration is within quantitation range of 0.2~4 mg/ml, and there are no interfering components)

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Cu I
- **Cu II** (when Cu concentration is below quantitation range)

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Cu II
- **Fe**

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Fe
- Mg

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Mg
- **Mn**

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Mn
- Pb

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Pb
- **Zn I** (when Zn concentration is within quantitation range of 0.05~1 mg/ml, and there are no interfering components)

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Zn I
- **Zn II** (when Zn concentration is below quantitation range)

  Same as that described in item 10.1.3 Flame Atomic Absorption Method, Zn II

# ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

## Section 7

**Cement Analysis**

**Ceramic Materials Analysis**

**Glass Analysis**

SHIMADZU CORPORATION
KYOTO, JAPAN

### Atomic Absorption Spectrophotometer Cookbook

### Section 7

## Table of Contents

# Introduction

Cookbook Section 7 describes the methods used for analysis of cement, ceramic materials and glass. These analysis methods, specified by the Japan Industrial Standards, are among those specified for elements to be analyzed by the atomic absorption method. This includes both those which have been modified to provide the optimum method when using a Shimadzu atomic absorption spectrophotometer, and for elements which are normally analyzed by other methods (techniques) for analyzing these elements using the atomic absorption method.

These analysis methods assume that the sample compositions conform to those specified in the Japan Industrial Standards, but for cases in which the actual sample compositions are not as specified in the Japan Industrial Standards, the pretreatment method, interference at the time of measurement, background absorption, and flame conditions may not necessarily be applicable.

In addition, the measurement conditions provided here are appropriate when using an AA-6000 Series Atomic Absorption Spectrophotometer. When using another atomic absorption spectrophotometer, the calibration curve, concentration range, and measurement conditions must be corrected.

# 12. Cement Analysis

## 12.1 Portland Cement Analysis Method

**Reference materials:**

Japan Industrial Standard, Portland Cement Chemical Analysis Method, JIS R 5202

### 12.1.1 Sample Pretreatment

**a) Perchloric acid dissolution**

Place 1 g of sample in a 100ml beaker, and add 10 ml of perchloric acid (60%). Then stir with a glass rod to dissolve. Heat over a sand bath to vaporize any moisture, (taking care not to allow any of the contents to spatter out), until the white fumes of perchloric acid are generated. At that point, cover with a watch glass and continue heating for 5 minutes longer. After allowing to cool, wash the watch glass and remove it. Add 5 ml of hydrochloric acid (1+1) and 20 ml of warm water, and mix the contents, crushing any large jelly-like lumps. Then pass the mixture through filter paper (type 5, B) into a 500 ml beaker, and wash 10~12 times with warm water. After cooling to room temperature, transfer filtrate and wash liquid to a 250 ml volumetric flask, adding water to bring this up to volume. This will serve as the measurement solution.

**Remark**: This solution is to be used for measurement of Al, Ca, Fe, K, Mg, Mn and Na.

**b) Hydrochloric acid dissolution**

Place 1 g of sample in a 200 ml beaker, and add 20 ml of water. Stir well with the tip of a glass rod, and add hydrochloric acid (1+1) to dissolve. At this time, if the sample is too difficult to dissolve, warm it a little and crush any lumps, which have not yet dissolved. Add warm water to approximately 50 ml, cover with a watch glass, and heat on a water bath for 10 minutes. Then pass through filter paper (type 5, B), washing 8 times with warm water. After cooling to room temperature, transfer filtrate and wash liquid to a 250 ml volumetric flask. Add water to bring this up to volume. This will serve as the measurement solution.

**Remark:** This solution is to be used for measurement of Ti.

### 12.1.2 Flame Atomic Absorption Method

**a) Target elements**

Al, Ca, Fe, K, Mg, Mn, Na, Ti

**b) Measurement procedures**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al**

**Reagents:**

Al standard solution (500 μg of Al/ml): Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Introduce an appropriate amount of sample solution pretreated using method b) (containing 0.5~10 mg of Al) into a 100 ml volumetric flask, and bring up to volume using hydrochloric acid (1+50). At this time, for a blank test, perform the same pretreatment on water as that used for the sample. Introduce the same volume of this solution as that of the sample solution into a 100 ml volumetric flask, and bring up to volume using hydrochloric acid (1+50). The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 1~20 ml of the Al standard solution (500 μg of Al/ml) into 100 ml volumetric flasks, and add hydrochloric acid to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 309.3 nm

Calibration curve concentration range: 5~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 2)

Calculation is for aluminum oxide ($Al_2O_3$)

Multiply value obtained for Al by 1.89.

- **Ca**

**Reagents:**

1) Ca standard solution (10 μg of Ca/ml): Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 g/l) : Dissolve 67 g of lanthanum chloride by adding small quantities of hydrochloric acid (1+1) little by little, and then add water up to a volume of 500 ml.

**Procedure:**

1) Place a suitable volume of sample pretreated using method a) (containing 5~150 μg of Ca) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then, after adding 3 ml of La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for correction of the value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 1~30 ml of the Ca standard solution (10 μg of Ca/ml) into 50 ml volumetric flasks. Add 3 ml of lanthanum solution (50 g/l) to each flask, and add water to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.2~6 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 9)

Calculation is for calcium oxide (CaO)

Multiply value obtained for Ca by 1.40.

- **Fe**

**Reagents:**

Fe standard solution (10 μg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The sample pretreated using method a) may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in sample measurement.
2) For the calibration curve, introduce 3~60 ml of Fe standard solution (10 μg of Fe/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement:**

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.3~6 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16).

Calculation is for diiron trioxide ($Fe_2O_3$)

Multiply value obtained for Fe by 1.43.

- **Mg**

**Reagents:**

1) Mg standard solution (5 μg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 μg/l) : Same as item 2) for •Ca reagent

**Procedure:**

1) Place a suitable volume of sample pretreated using method a) (containing .2~2.5 μg of Mg) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then add 3 ml of La solution (50 g/l),and bring up to volume with water. The measurement value obtained with this solution is used for the

correction value obtained with the actual sample.

2) For the calibration curve, place stepwise increments of 0.5~5 ml of the Mg standard solution (5 μg of Mg/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and add water to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: .05~0.5 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

Calculation is for magnesium oxide (MgO)

Multiply value obtained for Mg by 1.66.

- **Mn**

**Reagents:**

Mn standard solution (10 μg of Mn/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Dilute the sample pretreated using method a) with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in sample measurement.

2) For the calibration curve, place 2~40 ml of Mn standard solution (10 μg of Mn/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring up to volume with water.

Measurement:

wavelength: 279.5 nm

Calibration curve concentration range: 0.2~4 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 23).

Calculation is for manganese oxide (MnO)

Multiply value obtained for Mn by 1.29.

- **Ti**

**Reagents:**

1) Ti standard solution (500 μg of Ti/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Ammonium fluoride (50 g/l) : Dissolve 50 g of ammonium fluoride in water and bring up to a volume of 1000 ml.

**Procedure**:

1) Either use the sample pretreated via method b) directly, or dilute the pretreated sample with hydrochloric acid (1+50) so that its concentration is within the quantitation range. Add ammonium fluoride until its concentration reaches 2 g/l. This solution is used for measurement. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Then measure this solution. The obtained value may be used for the correction of the sample measurement.
2) For the calibration curve, place 1~20 ml of Ti standard solution (500 μg of Ti/ml) in stepwise volumes in 100 ml volumetric flasks. Add 4 ml of ammonium fluoride (50 g/l) and bring the solutions up to volume with hydrochloric acid (1+50). Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 364.3 nm

Calibration curve concentration range: 5~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 4).

Calculation is for titanium dioxide ($TiO_2$)

Multiply value obtained for Ti by 1.67.

- **K, Na**

**Reagents:**

1) K standard solution (1000 μg of K/ml)
2) Na standard solution (1000 μg of Na/ml)

   For preparation of 1) and 2), refer to Cookbook Section 2, item 3 Preparing Standards.
3) Alkali stock solution (K, Na each 500 μg/ml) : Mix together 500 ml each of K standard solution (1000 μg of K/ml) and Na standard solution (1000 μg of Na/ml).
4) Calcium stock solution (64 mg of CaO/ml) : To 114.3 g of calcium carbonate, add 300 ml of water and 600 ml of perchloric acid (60%) to dissolve. After this cools to room temperature, transfer to a 1000 ml volumetric flask, and bring up to volume with water.
5) Alkali mixed stock solutions : mix the alkali stock solution and the calcium stock solution in the ratios given in the following table, and then bring each of the solutions up to a volume of 1000 ml with water.

| Mixed standard solution no. | Alkali stock (ml) | Calcium stock (ml) | K, Na amount (mg) |
|---|---|---|---|
| 1 | 100 | 100 | 50 |
| 2 | 75 | 100 | 37.5 |
| 3 | 50 | 100 | 25 |
| 4 | 25 | 100 | 12.5 |
| 5 | 10 | 100 | 5 |
| 6 | 0 | 100 | 0 |

**Procedure:**

1) a) Introduce a suitable amount of sample pretreated using method a) (containing 0.2~2 mg each of K and Na) into a 50 ml volumetric flask, and add hydrochloric acid (1+50) to bring up to volume. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Transfer the same volume as that used for the sample to a 50 ml volumetric flask, bring up to volume with hydrochloric acid (1+50), and then measure this solution. The obtained value may be used for the correction value obtained in sample measurement.

2) For the calibration curve, dilute the alkali mixed stock solutions with hydrochloric acid (1+50) by a factor of 25. Use these to generate the calibration curve.

**Measurement:**

**1) K**

Measurement wavelength: 766.5 nm

Calibration curve concentration range: 0.2~2 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 19).

Remark: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

**2) Na**

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 0.2~2 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 24).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

Calculation is for potassium oxide ($K_2O$)

Multiply value obtained for K by 1.20.

Calculation is for sodium oxide ($Na_2O$)

Multiply value obtained for Na by 1.35.

## 12.2 Fireproof Brick and Fireproof Mortar Analysis Method

**Reference material:**

Japan Industrial Standards, Fireproof Brick and Fireproof Mortar Chemical Analysis Method, JIS R 2212

### 12.2.1 Sample Pretreatment

**a) Viscous fireproof brick and viscous fireproof mortar**

- Fe, Ti (Same pretreatment methods as used in Si weight absorptiometric combined method, Al EDTA- zinc back titration method)

1) Weigh out 0.5 g of sample in a platinum dish, and mix in 2 g of sodium carbonate (anhydrous). Begin heating at a low temperature, and gradually raising the temperature. Finally heat at 1100°C in an electric furnace for 10 minutes to melt. After cooling, cover with watch glass. Add 20 ml of hydrochloric acid (1+1) and 1 ml of sulfuric acid (1+1) and heat on a water bath to dissolve. Wash the watch glass and remove, and continue heating until dry.

2) After cooling, add 5 ml of hydrochloric acid, and let stand for about 1 minute. Add 20 ml of hot water and heat on a water bath for 5 minutes to dissolve all the soluble salts. Add a suitable amount of powdered filter paper and mix. Filter using type 5 filter paper (B). Wash several times with hot hydrochloric acid (1+50), and keep washing with hot water until a hydrogen ion reaction is no longer evident. Store the filtrate and wash liquid in a 300 ml beaker.

3) Transfer the precipitate and filter paper to a platinum crucible, and add 1 drop of sulfuric acid (1+1). Heat first at low temperature to ash the filter paper, and then heat at approximately 1100°C for 1 hour. After cooling in a desiccator, weigh, and repeat heating until the weight becomes stable. (X)

Wet the impure dioxide compounds with water, and add 3 drops of sulfuric acid (1+1). Then add 10 ml of hydrofluoric acid, and heat on a sand bath to dry. Heat at 1100°C for 5 minutes, cool in a desiccator and weigh. (Y) [Subtract weight (Y) from weight (X), and take that as the concentration of the main dioxide compounds. Determine the amount of the remaining dioxide compounds in the filtrate and wash liquid from step 2) by using the molybdenum blue absorptiometric method. The sum of this, with that of the main dioxide compounds, is considered the total weight of the dioxide compounds.]

Add 1 g of potassium disulfate to the remaining material in the crucible, and melt at 1100°C. After cooling, dissolve in water, add the filtrate, and wash liquid from step 2). Transfer to a 250 ml volumetric flask and bring up to volume with water. Use this for measurement of Al, Fe and Ti.

- **Ca, K, Mg, Na**

Weigh out 0.2 g of sample in a platinum dish, and wet with water. Add 5 ml of perchloric acid, 2 ml of nitric acid and 10 ml of hydrofluoric acid. Mix well with a platinum wire, and carefully heat on a sand bath to decompose. This will drive off all the intense white fumes of the perchloric acid until dry.

After cooling, add 5 ml of hydrochloric acid (1+1) and 10 ml of water, and cover with a watch glass. Heat on a water bath for about 10 minutes. After cooling, wash the watch glass and remove it. Transfer to a 100 ml volumetric flask. Add 10 ml of lanthanum chloride solution (50 g/l) and bring up to volume using water.

- **Mn**

Weigh out 0.5 g of sample in a platinum dish, and wet with water. Add 3 ml of sulfuric acid (1+1) and 10 ml of hydrofluoric acid. Mix well with a platinum wire, and carefully heat on a sand bath to decompose. This will drive off all the intense white fumes of the sulfuric acid until dry. After cooling, wash the inside walls of the platinum dish with water, and add 1 ml of sulfuric acid (1+1) and heat again until dry.

Add 2.5 g of sodium carbonate and 0.5 g of boric acid. Begin heating at a low temperature and gradually increase the temperature up to about 1000°C. Heat for about 10 minutes to melt. After cooling, add 10 ml of hydrochloric acid (1+1). Heat on a water bath and then add water to a volume of 100 ml.

**b) Silica brick and silica fireproof mortar**

- **Al, Ca, Fe, K, Mg, Na, Ti**

Weigh out 1 g of sample in a platinum dish, and wet with water. Add 5 ml of perchloric acid, 2 ml of nitric acid, and 15 ml of hydrofluoric acid. Mix well with a platinum wire, and carefully heat on a sand bath to decompose (driving off all the intense white fumes of the perchloric acid until dry). After cooling, add 5 ml of hydrochloric acid (1+1) and 10 ml of water. Cover with a watch glass and heat on a water bath for about 10 minutes. After cooling, wash the inside walls of the platinum dish with water, add 5 ml of hydrofluoric acid and heat again, driving off the white fumes until dry.

After cooling, add 25 ml of hydrochloric acid (1+1), cover with a watch glass, and heat on a water bath to dissolve. After cooling, transfer to a 250 ml volumetric flask and bring up to volume with water.

- **Mn**

a) The pretreatment is the same as that described in item a) Viscous fireproof brick and viscous fireproof mortar of Mn.

### c) High alumina fireproof brick and high alumina fireproof mortar

- **Fe, Ti** (Same pretreatment methods as used in Si dehydrated weight absorptiometric combined method, Al EDTA- zinc back titration method)

1) Weigh out 0.5 g of sample in a platinum dish, and mix in 3 g of sodium carbonate (anhydrous) and 1 g of boric acid. After mixing, begin heating at a low temperature, gradually raising the temperature, and finally heat at 1100°C in an electric furnace for 10 minutes to melt. After cooling, cover with watch glass, add 20 ml of hydrochloric acid (1+1) and 1 ml of sulfuric acid (1+1) and heat on a water bath to dissolve. Wash the watch glass and remove. Continue heating to volatilize. Just before evaporating to dryness, remove from the water bath, add 20 ml of methanol and carefully heat on the water bath until dry. During this heating period, use the flattened tip of a glass rod to pulverize any formed salt particles.
2) The rest of the pretreatment procedure is the same as that described in a) Viscous fireproof brick and viscous fireproof mortar, •Fe, Ti.

- **Ca, K, Mg, Na**

Weigh out 0.2 g of sample in a platinum cup, and wet with water. Add 5 ml of perchloric acid, 2 ml of nitric acid and 10 ml of hydrofluoric acid. Mix well with a platinum wire, and carefully heat on a sand bath to decompose, driving off all the intense white fumes of the perchloric acid until dry. After cooling, wash the inside walls of the platinum cup with water. Add 5 ml of perchloric acid, 2 ml of nitric acid and 10 ml of hydrofluoric acid, and again heat to drive off the white fumes of the perchloric acid until dry. After cooling, wash the inside walls of the platinum cup with water, add 3 ml of perchloric acid, and again heat until the white fumes are generated. When it comes close to drying, complete the drying at a lower temperature.

Next, add 5 ml of hydrochloric acid (1+1) and about 10 ml of water. Cover with a watch glass and heat on a water bath for 10 minutes. Wash the watch glass and remove it, and filter the remaining contents using type 6 filter paper. Then transfer to a 100 ml volumetric flask, add 10 ml of lanthanum chloride solution (50 g/l), and bring up to volume with water.

- **Mn**

a) The pretreatment is the same as that described in item a) Viscous fireproof brick and viscous fireproof mortar of Mn.

### d) Magnesia brick and magnesia fireproof mortar

- **Al, Ca, Fe** (Same pretreatment methods as used in Si perchloric acid dehydrated weight method, Al EDTA- zinc back titration method)

1) Weigh 1 g of sample into a 200 ml beaker, and wet with water. Add 10 ml of hydrochloric acid and 10 ml of perchloric acid and heat gradually on a sand bath to dissolve the sample. Continue heating, and when dense fumes of perchloric acid begin to be generated, cover with a

watch glass and continue heating for 10 minutes longer. After cooling, add about 50 ml of warm water and 5 ml of hydrochloric acid (1+1), and heat on a water bath to dissolve all the soluble salts. Filter using type 5 B filter paper. Then first wash with hydrochloric acid (1+50) several times, and then wash with hot water until a hydrogen ion reaction is no longer evident. Store the filtrate and wash liquid in a beaker.

2) Transfer the precipitate and filter paper to a platinum crucible. Add 1 drop of sulfuric acid (1+1), heat first at low temperature to ash the filter paper. Then heat at approximately 1100°C for 1 hour. After cooling in a desiccator, weigh, and repeat heating until the weight becomes stable. (X)

3) Wet the impure dioxide compounds with water. Add 3 drops of sulfuric acid (1+1) and 10 ml of hydrofluoric acid, and heat on a sand bath to dry. Heat at 1100°C for 5 minutes, then cool in a desiccator and weigh. (Y) [Subtract weight (Y) from weight (X), and take that as the concentration of the dioxide compounds. As for the remaining material in the crucible, add 1 g of sodium disulfate, and melt by heating at about 1100°C. After cooling, dissolve in warm water. Add this to the filtrate and wash liquid of step 2). Transfer this solution to a 250 ml volumetric flask and bring up to volume with water.]

e) Chrome / magnesia fireproof brick and chrome / magnesia fireproof mortar

- **Ca, Fe** (Same pretreatment as in Si perchloric acid dehydrated weight method and Al weight method)

1) Weigh 0.5 g of sample into a platinum crucible and add 4 g of sodium carbonate (anhydrous) and 1 g of boric acid. Begin heating at a low temperature and gradually increase the temperature up to about 1000°C. Continue heating for 30~60 minutes to melt. After cooling, transfer the entire crucible to a 200 ml beaker, cover with a watch glass. Gradually add 50 ml of warm water, 10 ml of sulfuric acid (1+1) and 20 ml of perchloric acid. Heat on a water bath to dissolve. Wash out the crucible, heat on a water bath until the white fumes of perchloric acid are generated, and then cover with a watch glass. Heat while the white fumes are generated intensely for 10 minutes.

2) After cooling, carefully add 50 ml of water and 5 ml of hydrochloric acid (1+1). Heat on a water bath for about 10 minutes to dissolve all soluble salts. Filter it using type 5 B filter paper, and wash several times with hot hydrochloric acid (1+50). Then wash with hot water until a hydrogen ion reaction is not evident. Store the filtrate and wash liquid in a 300 ml beaker.

3) The remainder of the pretreatment procedure is the same as that described in item a) Viscous fireproof brick and viscous fireproof mortar, •Fe, Ti.

### 12.2.2 Flame Atomic Absorption Method

**a) Target elements**

Al, Ca, Fe, K, Mg, Mn, Na, Ti

**b) Measurement procedure**

Measurement is conducted using the following procedure: The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al**

  Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Al.

- **Ca, Mg, K, Na** (viscous fireproof brick and viscous fireproof mortar, high alumina fireproof brick and high alumina fireproof mortar)

**Reagents**:

1) Ca standard solution (500 μg of Ca/ml)
2) Mg standard solution (100 μg of Mg/ml)
3) Na standard solution (500 μg of Na/ml)
4) K standard solution (500 μg of K/ml)

   For preparing reagents 1) ~ 4), please refer to Cookbook Section 2, Item 3 Preparing Standards.

5) La solution (50 g/l) : Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent 2).
6) Aluminum chloride solution : Weigh out 1.75 g of metallic aluminum (at least 99.9%), add 50 ml of hydrochloric acid (1+1) and heat to dissolve. Transfer to a 500 ml volumetric flask and bring up to volume with water.
7) Standard mixed solution series : Introduce Ca standard solution (500 μg of Ca/ml), Mg standard solution (100 μg of Mg/ml), Na standard solution (500 μg of Na/ml) and K standard solution (500 μg of K/ml) in stepwise fashion into 100 ml volumetric flasks as indicated in the following table. To each, add 10 ml of aluminum chloride solution, 10 ml of La solution (50 g/l) and 4 ml of hydrochloric acid (1+1). Bring all the solutions up to volume with water.

## Standard Mixed Solution Series Example

| Standard Mixed Solution Series | Aluminum Chloride Solution Addition Volume (ml) | Lanthanum Chloride Solution Addition Volume (ml) | Hydrochloric Acid (1+1) Addition Volume (ml) | Calcium Standard Solution | | Magnesium Standard Solution | | Sodium Standard Solution | | Potassium Standard Solution | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Standard Solution Addition Volume (ml) | Concen-tration (mg/100 ml) | Standard Solution Addition Volume (ml) | Concen-tration (mg/100 ml) | Standard Solution Addition Volume (ml) | Concen-tration (mg/100 ml) | Standard Solution Addition Volume (ml) | Concen-tration (mg/100 ml) |
| 1 | 10 | 10 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 10 | 10 | 4 | 1.0 | 0.5 | 1.0 | 0.1 | 1.0 | 0.5 | 1.0 | 0.5 |
| 3 | 10 | 10 | 4 | 2.0 | 1.0 | 2.0 | 0.2 | 2.0 | 1.0 | 2.0 | 1.0 |
| 4 | 10 | 10 | 4 | 3.0 | 1.5 | 3.0 | 0.3 | 3.0 | 1.5 | 3.0 | 1.5 |
| 5 | 10 | 10 | 4 | 4.0 | 2.0 | 4.0 | 0.4 | 4.0 | 2.0 | 4.0 | 2.0 |
| 6 | 10 | 10 | 4 | 5.0 | 2.5 | 5.0 | 0.5 | 5.0 | 2.5 | 5.0 | 2.5 |
| 7 | 10 | 10 | 4 | 6.0 | 3.0 | 6.0 | 0.6 | 6.0 | 3.0 | 6.0 | 3.0 |
| 8 | 10 | 10 | 4 | 7.0 | 3.5 | 7.0 | 0.7 | 7.0 | 3.5 | 7.0 | 3.5 |
| 9 | 10 | 10 | 4 | 8.0 | 4.0 | 8.0 | 0.8 | 8.0 | 4.0 | 8.0 | 4.0 |
| 10 | 10 | 10 | 4 | 9.0 | 4.5 | 9.0 | 0.9 | 9.0 | 4.5 | 9.0 | 4.5 |

**Procedure**:

1) a) The •Ca, K, Mg and Na sample solutions, pretreated according to a) Viscous fireproof brick and viscous fireproof mortar or c) High alumina fireproof brick and high alumina fireproof mortar, can be measured directly or after diluting with hydrochloric acid (1+50) according to the concentration ranges indicated in the standard mixed solution series. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample. Using the same dilution factor, and use the value obtained to correct the measurement value obtained with the sample.
2) Generate a calibration curve using 3~5 points from the standard mixed solution series.

**Measurement:**

1) Ca

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 5~44 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 9).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

**2) Mg**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: 1~9 µg/ml measurement conditions: Refer to Cookbook Section 3, Item 6.4, 22).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle in the same way as that for Ca.

**3) K**

Measurement wavelength: 766.5 nm

Calibration curve concentration range: 5~45 μg/ml

measurement conditions: Refer to Cookbook Section 3, Item 6.4, 19).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle in the same way as that for Ca.

**4) Na**

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 5~45 μg/ml

measurement conditions: Refer to Cookbook Section 3, Item 6.4, 24).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle in the same way as that for Ca.

Calculation is for calcium oxide (CaO)

Multiply value obtained for Ca by 1.40.

Calculation is for magnesium oxide (MgO)

Multiply value obtained for Mg by 1.66.

Calculation is for potassium oxide ($K_2O$)

Multiply value obtained for K by 1.20.

Calculation is for sodium oxide ($Na_2O$)

Multiply value obtained for Na by 1.35.

- **Ca, Mg, K, Na** (silica brick and silica fireproof mortar)

**Reagents:**

Same as those described for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar)

**Procedure:**

1) Introduce 50 ml of the •Al, Ca, Fe, K, Mg, Na and Ti sample solution, pretreated according to b) Silica brick and silica fireproof mortar, into a 100 ml volumetric flask. Add 10 ml of lanthanum chloride solution (50 g/l), and bring up to volume with hydrochloric acid (1+50). This solution can be measured directly or after diluting with hydrochloric acid (1+50) according to the concentration ranges indicated in the standard mixed solution series. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample using the same dilution factor. Use the value obtained to correct the measurement value obtained with the sample.

2) Generate a calibration curve using 3~5 points from the standard mixed solution series, as described for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar).

Measurement:

Use the same procedure as that for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar), 1) Ca, 2) Mg, 3) K and 4) Na.

- **Ca** (magnesia brick and magnesia fireproof mortar, chrome/magnesia brick and chrome/magnesia mortar)

Reagents:

Same as those used for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar).

**Procedure:**

1) Introduce into a 100 ml volumetric flask 50 ml of the •Al, Ca, Fe sample solution, pretreated according to d) Magnesia brick and magnesia fireproof mortar, or •Ca, Fe sample solution pretreated according to e) Chrome / magnesia fireproof brick and chrome / magnesia fireproof mortar. Add 10 ml of lanthanum chloride solution (50 g/l) and bring up to volume with hydrochloric acid (1+50). This solution can be measured directly or after diluting with hydrochloric acid (1+50) according to the concentration ranges indicated in the standard mixed solution series.
2) Generate a calibration curve using 3~5 points from the standard mixed solution series, as described for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar).

**Measurement:**

Use the same procedure as that for •Ca, Mg, K, Na (viscous fireproof brick and viscous fireproof mortar), 1) Ca.

- **Fe**

Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Fe.

- **Mn**

Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Mn.

- **Ti**

Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ti.

## 12.3 Analysis Method for Aluminum Cement for Fireproof Materials

**Reference materials:**

Japan Industrial Standards, Fireproof Aluminum Cement Chemical Analysis Method, JIS R 2522

### 12.3.1 Sample Pretreatment

**a) Fireproof aluminum cement Type 1 and Type 2**

- **Fe, Si, Ti**

Weigh 1.0 g of sample into a platinum dish. Mix in 4 g of sodium carbonate (anhydrous) and 2 g of boric acid. Begin heating at a low temperature, gradually raising the temperature, and finally heat at 1100°C in an electric furnace for 30 minutes to melt. Cover with watch glass and allow to cool. Add 40 ml of hydrochloric acid (1+1) and 1 ml of sulfuric acid (1+1). Heat on a water bath to dissolve, with solution becoming translucent. After cooling, wash the watch glass and remove it. Transfer the contents of the dish to a 250 ml volumetric flask, and bring up to volume with water.

- **Mg**

  Weigh out 0.1 g of sample and introduce it into a 100 ml beaker containing 10 ml of water. After thoroughly mixing, add 10 ml of hydrochloric acid (1+2), and heat on a water bath for about 50 minutes, intermittently mixing, until dissolved. Add about 20 ml of warm water, filter using type 5 B filter paper and wash with hot water. Transfer the filtrate and wash liquid to a 100 ml volumetric flask. Add 5 ml of La solution (50 g/l), and bring up to volume with water.

**b) Fireproof aluminum cement Type 3 and Type 4**

**Fe, Ti (**same pretreatment method as for Si dehydrated weight method)

1) Weigh 0.5 g of sample into a 200 ml beaker, and wet with water. Add 10 ml of hydrochloric acid (1+1) and 10 ml of perchloric acid. Cover with a watch glass and heat on a sand bath to decompose. After decomposition, wash the watch glass and inside walls of the beaker with water. Heat again on the sand bath, and when the white fumes of perchloric acid begin to be generated, cover with a watch glass and continue heating for 10 minutes longer. After cooling, add 50 ml of warm water and 5 ml of hydrochloric acid (1+1), and heat on a water bath to dissolve all the soluble salts. Filter using type 5 B filter paper, and after washing several times with warm hydrochloric acid (1+50), wash with hot water until a hydrogen ion reaction is no longer evident. Store the filtrate and wash liquid in a beaker.

2) Transfer the precipitate and filter paper to a platinum crucible. After drying, heat first at low temperature to ash the filter paper. Then heat at 1050~1100°C for 1 hour. After cooling in a desiccator, weigh, and repeat heating until the weight becomes stable. (X)

3) Wet the weighed precipitate (impure dioxide compounds) with water. Add 3 drops of sulfuric acid (1+1) and 10 ml of hydrofluoric acid. Heat on a sand bath to dry. Heat at 1050~1100°C for 5 minutes, and cool in a desiccator and weigh.(Y) [Subtract weight (Y) from weight (X), and take that as the concentration of the dioxide compounds.] Add 1 g of potassium disulfate to the remaining material in the crucible, and heat to melt. After cooling, add 10 ml of water and 5 ml of hydrochloric acid (1+1). Heat to dissolve, and then add the filtrate and wash liquid from step 1). Transfer to a 250 ml volumetric flask and bring up to volume with water.

- Mg

  Follow the same pretreatment procedure as that described in a) Fireproof aluminum cement Type 1 and Type 2, Mg.

12.3.2 Flame Atomic Absorption Method

a) Target elements

Fe, Mg, Si, Ti

**b) Measurement procedure**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Fe** (Standard Addition Method)

**Reagents:**

Fe standard solution (10 µg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Introduce appropriate amounts of pretreated Fe sample solution (containing 10~100 µg of Fe) into 50 ml volumetric flasks. To one of the flasks add no Fe standard solution, and to the others, add 5~25 ml of the Fe standard solution (10 µg of Fe/ml) in at least 3 incremental volumes. Then add hydrochloric acid (1+1) so that the acid concentration of each becomes 0.5 mol/l. Then bring all the solutions up to volume with water. These solutions are used for measurement.

   For a blank test, pretreat the reagent using the same procedure as that used on the sample, and introduce this solution into a 50 ml volumetric flask in the same volume as the sample. Add hydrochloric acid so that the acid concentration becomes 0.5 mol/l, and use this solution for blank sample measurement.

2) Generate a calibration curve using the signals from the measurement of the solutions of step 1). After verifying its linearity, use this to extrapolate the Fe concentrations in the samples.

Measurement:

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.1~5 µg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 16

Calculation is for diiron trioxide ($Fe_2O_3$)

Multiply value obtained for Fe by 1.43.

- **Mg**

**Reagents:**

1) Mg standard solution (10 μg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Aluminum solution (6.6 mg $Al_2O_3$/ml) : Add 50 ml of hydrochloric acid (1+1) to 1.75 g of aluminum chloride. Heat to dissolve. After cooling, add water to bring up to 500 ml.

3) La solution (50 g/l) : Same as item 12.1.2 Flame Atomic Absorption Method, •Ca reagent, 2)

4) Standard mixed solution series : Introduce Mg standard solution (10 mg of Mg/ml) in stepwise fashion into 100 ml volumetric flasks as indicated in the following table. To each, add 10 ml of aluminum solution (6.6 mg $Al_2O_3$/ml), 5 ml of La solution (50 g/l) and 4 ml of hydrochloric acid (1+1). Then bring all the solutions up to volume with water.

**Standard Mixed Solution Series Example**

| | Aluminum Solution (ml) | La Solution (ml) | Hydrochloric Acid (1+1) (ml) | Magnesium Standard Solution (ml) | Magnesium Concentration (mg/100 ml) |
|---|---|---|---|---|---|
| 1 | 10 | 5 | 4 | 0 | 0 |
| 2 | 10 | 5 | 4 | 3 | 0.3 |
| 3 | 10 | 5 | 4 | 6 | 0.6 |
| 4 | 10 | 5 | 4 | 9 | 0.9 |
| 5 | 10 | 5 | 4 | 12 | 1.2 |

**Procedure:**

1) The pretreated sample solutions of a) or b), •Mg, may be used directly, or after dilution with hydrochloric acid (1+50) within the concentration range of the standard mixed solution series. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample. Using the same dilution factor, and use that value to correct for the measurement value obtained with the sample.

2) The standard curve is generated by measuring 3~5 points from the standard mixed solution series.

**Measurement:**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: 3~12 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

Calculation is for magnesium oxide (MgO)

Multiply value obtained for Mg by 1.66.

- Si

**Reagents:**

Si standard solution (1000 µg of Si/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**

1) The pretreated sample solution of step a) may be used directly, or may be used for measurement after diluting with hydrochloric acid (1+50) so that it falls within the calibration curve concentration range. At this time, for the blank test, pretreat the reagent using the same procedure as that for the sample, and use the value obtained in this measurement to correct the value obtained in sample measurement.
2) For the calibration curve, introduce 1~10 ml of Si standard solution (1000 µg of Si/ml) into 100 ml volumetric flasks in incremental volumes. After adding acid using the same conditions as that for the sample, bring up to volume with water. Measure these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 251.6 nm

Calibration curve concentration range: 10~100 µg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 34).

Calculation is for silicon dioxide ($SiO_2$)

Multiply value obtained for Si by 2.13.

- **Ti**

The procedure is the same as that described in item 12.1.2 Flame Atomic Absorption Method of Ti.

# 13. Ceramic Materials Analysis

## 13.1 Nitride Compound Powder Analysis Method

**Reference materials:**

Japan Industrial Standards, Nitride Compound Powder Chemical Analysis Method JIS R 1603

### 13.1.1 Sample Pretreatment

Weigh 0.5 g of sample into a platinum crucible (No. 20). Place this in the resin cup of the pressure decomposition container displayed in the following figure. Add 1 ml of nitric acid and 10 ml of perchloric acid. Cover this with the middle cap and place in the pressure resistant container. Then cover with the external cap, screwing on tightly. Place in an air bath adjusted to 160 ± 5°C, and heat overnight. After cooling, remove the screw cap, and carefully remove the middle cap. Using plastic tweezers, remove the platinum crucible, and transfer the solution to a platinum dish. Wash the platinum crucible, tweezers, middle cap, and resin cup with a small amount of water. Collect the wash water also in the platinum dish.

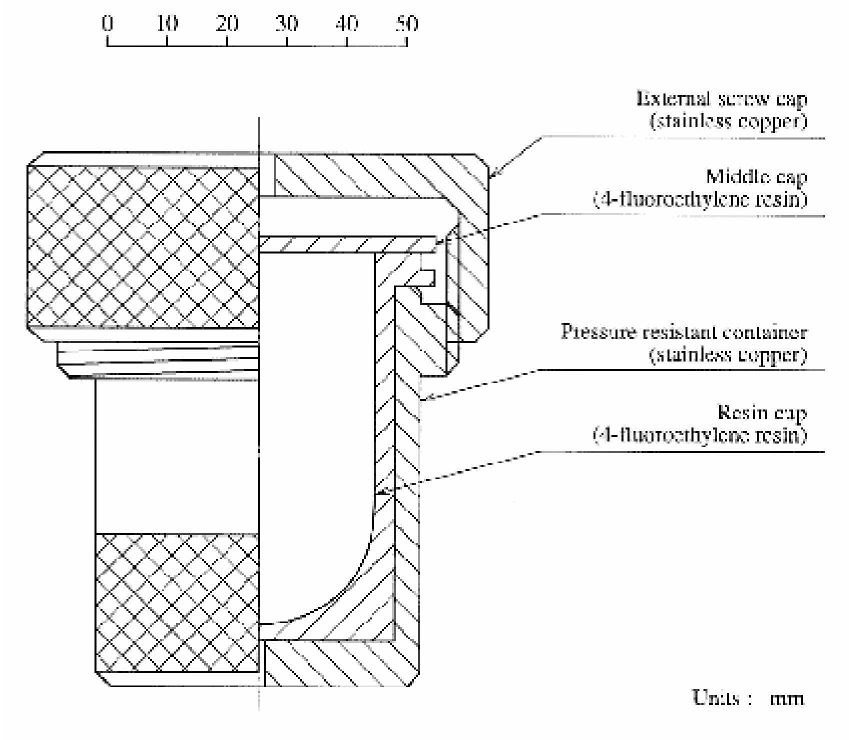


**Figure: Pressure Resistant Decomposition Container**

Add 3 ml of perchloric acid and heat on a sand bath until dry. After cooling, wash the inside walls of the platinum dish with a small amount of water. Add 1 ml of perchloric acid, and again heat on a sand bath until dry. Add 4 ml of hydrochloric acid (1+1) and 20 ml of water. Cover with a watch glass, and heat on a water bath to dissolve. Cool to room temperature, and then transfer to a 100 ml volumetric flask. Add 2 ml of La solution (50 g/l) and bring up to volume with water.

### 13.1.2. Flame Atomic Absorption Method

**a) Target elements**

Al, Fe, Ca

**b) Measurement procedure**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al, Fe, Ca**

**Reagents:**

1) Al standard solution (1000 µg of Al/ml)
2) Ca standard solution (500 µg of Ca/ml)
3) Fe standard solution (1000 µg of Fe/ml)

Prepare 1), 2) and 3) referring to Cookbook Section 2, Item 3 Preparing Standards

4) Mixed standard solution (100 µg Al + 100 µg Fe + 5 µg Ca/ml) : Accurately weigh 25 ml of Al standard solution, 25 ml of Fe standard solution and 2.5 ml of Ca standard

solution into a platinum dish. Add 2 ml of sulfuric acid (1+1) and heat on a sand bath to dry. Add 2 ml of hydrochloric acid (1+1) and 20 ml of water, and cover with a watch glass. Heat on a water bath to dissolve. After cooling, transfer to a 250 ml volumetric flask and bring up to volume with water.

5) La solution (50 g/l) : Same procedure as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent, 2).

**Procedure:**

1) The pretreated sample is used directly for measurement of Al, Ca and Fe. At this time, for a blank test, perform the same pretreatment used for the sample on a suitable amount of water. After cooling, transfer to a 100 ml volumetric flask. Add 2 ml of La solution (50 g/l), and bring up to volume with water. The value obtained in measurement of the blank can be used to correct the value obtained for the sample.

2) Generate a 3~5 point calibration curve using standard solutions having the Al, Ca and Fe ratios prepared as indicated in the following table.

| Mixed Standard Solution Series | La Solution Addition Volume (ml) | Hydrochloric Acid (1+1) Addition Volume (ml) | Mixed Standard Solution Addition Volume (ml) | Al | Standard Solution Concentrations (mg/ml) | Ca |
|---|---|---|---|---|---|---|
| 1 | 2 | 4 | 0 | 0 | 0 | 0 |
| 2 | 2 | 4 | 2 | 2 | 2 | 0.1 |
| 3 | 2 | 4 | 5 | 5 | 5 | 0.25 |
| 4 | 2 | 4 | 10 | 10 | 10 | 0.5 |
| 5 | 2 | 4 | 15 | 15 | 15 | 0.75 |
| 6 | 2 | 4 | 20 | 20 | 20 | 1.0 |
| 7 | 2 | 4 | 25 | 25 | 25 | 1.25 |
| 8 | 2 | 4 | 30 | 30 | 30 | 1.50 |

**Measurement:**

**1) Al**

Measurement wavelength: 309.2 nm

Calibration curve concentration range: 2~30 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 2).

**2) Ca**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.1~1.5 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 9).

**3) Fe**

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 2~30 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 16).

Remark: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

Calculation is for aluminum oxide ($Al_2O_3$)

Multiply value obtained for Al by 1.89.

Calculation is for calcium oxide (CaO)

Multiply value obtained for Ca by 1.40.

Calculation is for diiron trioxide ($Fe_2O_3$)

Multiply value obtained for Fe by 1.43.

## 13.2 Ground Alumina Analysis Method

**Reference materials:**

Japan Industrial Standards, Ground Alumina Analysis Method, JIS R 6123

### 13.2.1 Sample Pretreatment

**a) Fe, Ti**

Measure 3 g of anhydrous potassium carbonate and 2 g of boric acid into a platinum crucible. Heat over a burner to drive of all the moisture (after the anhydrous potassium carbonate and boric acid melt, immediately remove from the burner). To this, add about 0.5 g of sample, accurately weighed to the nearest 0.1 mg. Heat in an electric furnace at 950°C for 20 minutes to melt.

After cooling the melted material, transfer the entire crucible with its cover to a 300 ml beaker containing 100 ml of water and 30 ml of sulfuric acid (1+1), to completely dissolve the melted material. Wash the crucible and its cover with water, and then remove them from the beaker. Heat the beaker on a sand bath until the white fumes of sulfuric acid are generated, and then continue heating for 5~10 minutes longer.

After cooling, add 100 ml of water. Heat to dissolve all the soluble salts, then immediately filter through type 5 B filter paper. Collect the filtrate and wash liquid in a 250 ml volumetric flask, and bring up to volume with water. Use this solution for sample measurement.

**b) Ca, Mg**

Measure 3 g of anhydrous potassium carbonate and 2 g of boric acid into a platinum crucible. Heat over a burner to drive off all the moisture. To this, add about 0.5 g of sample, accurately weighed to the nearest 0.1 mg. Heat in an electric furnace at 950°C for 20 minutes to melt.

After cooling, transfer the melted material (along with the entire crucible and cover) to a 300 ml beaker containing 150 ml of warm water. Heat to dissolve the melted material in the crucible. Wash the crucible and its cover with water, and then remove them from the beaker. Heat the beaker on a water bath, and let it stand for a while. Then filter through type 5 B filter paper.

Wash several times with warm sodium carbonate solution (1% w/v), and discard the wash liquid. Dissolve the precipitate in the filter paper in 10~15 ml of warm hydrochloric acid (1+2), and wash with warm water. Discard the filter paper. Transfer this solution to a 250 ml volumetric flask, and bring up to volume with water. Use this solution for sample measurement.

**c) Na**

Pulverize the sample in a mortar until the particles cannot be felt with the fingertip. Introduce into a platinum crucible about 0.5 g of sample, accurately weighed to the nearest 0.1 mg. Add 1 g of boric acid and mix well. Then cover with another 0.5 g. Cover and heat in an electric furnace at 950°C to melt.

After cooling, transfer the melted material with the entire crucible and cover to a 300 ml beaker containing 100 ml of warm water. Heat on a water bath to dissolve the melted material in the crucible. Wash the crucible and its cover with water, and then remove them from the beaker. Use a glass rod to crush the melted material, and let it stand on a water bath for about 5 minutes. After cooling, transfer to a 250 ml volumetric flask, bring up to volume with water, and then shake the flask to mix. Filter through dry filter paper (type 5 C). Use this solution for sample measurement.

### 13.2.2 Flame Atomic Absorption Method

**a) Target elements**

Ca, Fe, Mg, Na, Ti

b) Measurement procedure

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Ca**

**Reagents:**

1) Ca standard solution (10 μg of Ca/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 g/l) : Same procedure as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent, 2).

**Procedure:**

1) Place a suitable volume of sample pretreated using method b) (containing 5~150 μg of Ca) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), and bring up to volume with water for measurement. At this time, for a blank test, using sample without any reagent, perform the same pretreatment as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then, after adding 3 ml of

La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.

2) For the calibration curve, place stepwise increments of 1~30 ml of the Ca standard solution (10 µg of Ca/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and add water to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.2~6 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 9)

Calculation is for calcium oxide (CaO)

Multiply value obtained for Ca by 1.40.

- **Fe**

**Reagents:**

Fe standard solution (10 µg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Dilute the sample pretreated using method a) with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in the sample measurement.

2) For the calibration curve, introduce 3~60 ml of Fe standard solution (10 µg of Fe/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring up to volume with water.

**Measurement:**

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.3~6 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16).

Calculation is for diiron trioxide ($Fe_2O_3$)

Multiply value obtained for Fe by 1.43.

- **Mg**

**Reagents:**

1) Mg standard solution (5 µg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) La solution (50 g/l) : Same as item 2) for •Ca reagent

**Procedure:**

1) Place a suitable volume of sample pretreated using method b) (containing .2~25 µg of Mg) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 µg/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment on the reagent containing no sample as that performed for the sample. Place the same volume of this solution in a 50 ml volumetric flask. Then add 3 ml of La solution (50 g/l), and bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 0.5~5 ml of the Mg standard into 50 ml volumetric flasks. Add 3 ml of La solution (5 µg/l) to each flask, and add water to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: .05~0.5 µg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

Calculation is for magnesium oxide (MgO)

Multiply value obtained for Mg by 1.66.

- **Ti**

**Reagents:**

1) Ti standard solution (100 µg of Ti/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Ammonium fluoride (50 g/l) : Dissolve 50 g of ammonium fluoride in water and bring up to a volume of 1000 ml.

Procedure:

1) Introduce sample pretreated via method a) (containing 0.2~3 mg of Ti) into a 50 ml volumetric flask. Add 5 ml of ammonium fluoride, and bring up to volume with water. This solution is used for measurement. At this time, for a blank test, perform the same pretreatment on reagent without sample as performed on the sample, and introduce the same amount of this solution as sample into a 50 ml volumetric flask. Add 5 ml of ammonium fluoride (50 g/l) and bring the solutions up to volume with water. The value obtained from the measurement of this solution may be used for the correction value obtained in the sample measurement
2) For the calibration curve, place 2~30 ml of Ti standard solution (100 µg of Ti/ml) in stepwise volumes in 50 ml volumetric flasks. Add 5 ml of ammonium fluoride (50 g/l) and bring the solutions up to volume with water. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 364.3 nm

Calibration curve concentration range: 10~70 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 41).

Calculation is for titanium dioxide ($TiO_2$)

Multiply value obtained for Ti by 1.67.

- **Na**

**Reagents:**

Na standard solution (5 μg of Na/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure**:

1) The sample pretreated using method c) may be used directly, or diluted so that its concentration is within the quantitation range. At this time, perform the same pretreatment on reagent containing no sample as that used for the sample. Then measure this solution. The obtained value may be used for the correction value obtained in the sample measurement.
2) For the calibration curve, introduce 1~10 ml of Na standard solution (5 μg of Na/ml) in stepwise volumes in 100 ml volumetric flasks. Bring these solutions up to volume with hydrochloric acid (1+100). Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 0.05~0.5 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 24).

Calculation is for sodium oxide ($Na_2O$)

Multiply value obtained for Na by 1.35.

## 13.3 Carbonized Compound Ground Materials Analysis Method

**Reference materials:**

Japan Industrial Standards, Carbonized Compound Ground Materials Chemical Analysis Method JIS R 6124

### 13.3.1 Sample Pretreatment

Place about 1.0 g of sample, weighed to the nearest 0.1 mg, in a platinum crucible. Add 10 ml of hydrofluoric acid, 1 ml of nitric acid, and 3 ml of perchloric acid. Heat on a sand bath until the white fumes of perchloric acid are generated. After cooling, transfer the sample along with the crucible to a 300 ml beaker containing 5 ml of hydrochloric acid (1+1) and 150 ml of warm water. Heat to dissolve all of the soluble salts in the crucible. Wash the crucible with sufficient water, and then remove the crucible. Filter through type 5 B filter paper. Wash the precipitate several times with hydrochloric acid

(1+100), and then with warm water until the there is no longer a chloride ion reaction evident. Transfer the filtrate and wash liquid to a 250 ml volumetric flask, and bring up to volume with water. Use this solution for measurement.

13.3.2 Flame Atomic Absorption Method

a) Target elements

Al, Ca, Fe, Mg,

**b) Measurement procedures**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al**

**Reagents:**

Al standard solution (500 µg of Al/ml): Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Introduce an appropriate amount of pretreated sample (containing 0.5~10 mg of Al) into a 100 ml volumetric flask. Bring up to volume using hydrochloric acid (1+50). Use this solution for sample measurement. At this time, for a blank test, perform the same pretreatment on water as that used for the sample. Introduce the same volume of this solution as that of the sample solution into a 100 ml volumetric flask, and bring up to volume using hydrochloric acid (1+50). The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 1~20 ml of the Al standard solution (500 µg of Al/ml) into 100 ml volumetric flasks. Add hydrochloric acid (1+50) to bring all the solutions up to volume. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 309.3 nm

Calibration curve concentration range: 5~100 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 2)

- **Ca**

**Reagents:**

1) Ca standard solution (10 µg of Ca/ml): Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 g/l) : Same procedure as described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent, 2)

**Procedure:**

1) Place a suitable volume of sample pretreated using method a) (containing 5~150 µg of Ca) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample, and place the same volume of this solution in a 50 ml volumetric flask. Then, after adding 3 ml of La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 1~30 ml of the Ca standard solution (10 µg of Ca/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and then add water to bring all the solutions up to volume. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.3~6 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 9)

- **Fe**

**Reagents:**

Fe standard solution (10 µg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

Procedure:

1) Dilute the sample pretreated using method with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in sample measurement.
2) For the calibration curve, introduce 3~60 ml of Fe standard solution (10 µg of Fe/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring all the solutions up to volume with water. Use these solutions to generate the calibration curve.

Measurement:

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.3~6 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16).

- **Mg**

**Reagents:**

1) Mg standard solution (5 µg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 µg/l) : Same as item 12.1.2, •Ca reagent, 2)

**Procedure:**

1) Place a suitable volume of pretreated sample using method a) (containing .2~25 µg of Mg) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for measurement. At this time, for a blank test, perform the same pretreatment on a suitable volume of water as that performed for the sample. Place the same volume of this solution in a 50 ml volumetric flask. Then add 3 ml of La solution (50 g/l), and bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
2) For the calibration curve, place stepwise increments of 0.5~5 ml of the Mg standard solution (5 µg of Mg/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and add water to bring all the solutions up to volume. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: .05~0.5 µg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

Reference materials:

Japan Industrial Standards, Lime Chemical Analysis Method JIS R 9011

### 13.4 Lime Analysis Method

**Reference materials:**

Japan Industrial Standards, Lime Chemical Analysis Method JIS R 9011

#### 13.4.1 Sample Pretreatment

Introduce about 1 g of sample, weighed to the nearest 0.1 mg, into a beaker. Add a small quantity of water to make a slurry, and cover with a watch glass. Add 10 ml of hydrochloric acid (1+1) and mix to dissolve all the soluble components. To this, add 15 ml of perchloric acid (60%) and heat on a sand bath until the white fumes of perchloric acid are generated. Continue heating for 10 minutes longer. After allowing it to cool a little, add 5 ml of hydrochloric acid (1+1) and 50 ml of warm water, and then mix. After the precipitate has sunk for the most part, filter through type 5 B filter paper and wash 10~12 times with warm water. Store the filtrate and wash liquid, and then mix with the solution prepared using the following procedure.

Transfer the filter paper with its remaining precipitate to a platinum crucible and dry. Gradually increase the temperature taking every precaution that it does not burst into flames, until the contents are completely ashed. To this add 2 or 3 drops of either sulfuric acid (1+1) or perchloric acid (60%), and then add 5 ml of hydrofluoric acid. Heat this in a ventilated room to volatilize the liquids. After the white fumes are driven off, add 1~2 g of sodium pyrosulfate (sodium bisulfate). Cover the crucible and heat with a weak flame until it becomes a dark red color, melting the remainder of the material. After cooling the crucible, add 10 ml of warm water and warm a little to dissolve the melted material. To this, add the filtrate and wash liquid from the above procedure, and add water to bring up to 250 ml. Use this solution for sample measurement.

### 13.4.2 Flame Atomic Absorption Method

a) Target elements

Al, Ca, Fe, Mg

b) Measurement procedure

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- Al

  Same as described in item 13.3.2 Flame Atomic Absorption Method, •Al
- **Ca**

  same as described in item 13.3.2 Flame Atomic Absorption Method, •Ca
- **Fe**

  Same as described in item 13.3.2 Flame Atomic Absorption Method, •Fe
- **Mg**

  Same as described in item 13.3.2 Flame Atomic Absorption Method, •Mg

## 13.5 Analysis Method for Chromium Ore for Fireproof Materials

Reference materials:

Chemical Analysis Method for Chromium Ore for Fireproof Materials JIS R 2901

### 13.5.1 Sample Pretreatment

Weigh 0.5 g of sample into a platinum dish, and mix in 4 g of sodium carbonate (anhydrous) and 2.7 g of boric acid. After mixing, begin heating at a low temperature, gradually raising the temperature, and finally heat at 1100°C in an electric furnace until the mixture is completely melted. Cover with a watch glass. After cooling, add 55 ml of sulfuric acid (1+9) and heat on a water bath, periodically mixing to dissolve. After cooling, wash the watch glass and remove. Then transfer to a 250 ml volumetric flask. Add water to bring up to volume.

### 13.5.2 Flame Atomic Absorption Method

**a) Target elements**

Mn, Si, Ti

**b) Measurement procedures**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Mn**

**Reagents:**

1) Mn standard solution (20 µg of Mn/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) La solution (50 g/l) : Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent 2).
3) Addition solution : Gradually add 55 ml of sulfuric acid (1+9) to 4 g of sodium carbonate (anhydrous) and 2.7 g of boric acid to dissolve. Add 50 ml of water and heat on a water bath. After cooling, add water to bring the solution up to 250 ml.

**Procedure:**

1) Introduce a suitable amount of sample (containing 10~200 µg of Mn) into a 50 ml volumetric flask. Add 5 ml of La solution (50 g/ml) and bring up to volume with water.
   At this time, introduce into a 50 ml volumetric flask the same amount of the addition solution as used for the sample solution. After adding 5 ml of La solution (50 g/l), bring up to volume with water. The value obtained from measurement of this solution may be used for the correction value obtained in sample measurement.
2) For the calibration curve, introduce 1~20 µl of Mn standard solution (20 mg of Mn/ml) in stepwise volumes into 50 ml volumetric flasks. After adding 5 ml of La solution and the addition solution in the same volume as that for the sample, bring up to volume with water. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 279.5 nm

Calibration curve concentration range: 0.2~4 µg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 23).

Calculation is for manganese oxide (MnO)

Multiply value obtained for Mn by 1.29.

- **Si**

**Reagents:**

1) Si standard solution (1000 µg of Si/ml) : Refer to Cookbook Section 2, item 3

Preparing Standards

2) Addition solution : Same as •Mn reagent, 3)

**Procedure:**

1) The pretreated sample solution may be used directly, or may be diluted with hydrochloric acid (1+50) so that it falls within the calibration curve concentration range.

   At this time, introduce into a 50 ml volumetric flask the same amount of the addition solution as used for the sample solution. At this time, for the blank test, add hydrochloric acid (1+50) to the addition solution using the same volumes for preparing the sample solution. Use the value obtained from measuring this solution to correct the value obtained in sample measurement.

2) For the calibration curve, introduce 0.5~5 ml of Si standard solution (1000 μg of Si/ml) into 50 ml volumetric flasks in incremental volumes. After adding the same volume of addition solution as that added to the sample, bring up to volume with hydrochloric acid (1+50). Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 251.6 nm

Calibration curve concentration range: 10~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 34).

Calculation is for silicon dioxide ($SiO_2$)

Multiply value obtained for Si by 2.13.

- **Ti**

**Reagents:**

1) Ti standard solution (1000 μg of Ti/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) La solution (50 g/l) : Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent 2).

3) Addition solution : Same as •Mn reagent, 3)

**Procedure:**

1) Introduce a suitable amount of sample (containing 0.5 mg of Ti) into a 50 ml volumetric flask. Add 5 ml of La solution (50 g/ml) and bring up to volume with water.

   At this time, introduce into a 50 ml volumetric flask the same amount of the addition solution as used for the sample solution. After adding 5 ml of La solution (50 g/l), bring up to volume with water. The value obtained from the measurement of this solution may be used for the correction value obtained in the sample measurement.

2) For the calibration curve, introduce 0.5~5 ml of Ti standard solution (1000 μg of Ti/ml) in stepwise volumes into 50 ml volumetric flasks. After adding 5 ml of La solution and the addition solution in the same volume as that for the sample, bring up to volume

with water. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 364.3 nm

Calibration curve concentration range: 10~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 4).

Calculation is for titanium dioxide ($TiO_2$)

Multiply value obtained for Ti by 1.67.

## 14. Glass Analysis

### 14.1 Soda Lime Glass Analysis Method

**Reference materials:**

Japan Industrial Standard, Soda Lime Glass Analysis Method, JIS R 3101

### 14.1.1 Sample Pretreatment

Weigh 1 g of sample into a platinum dish, and moisten with about 1 ml of water. Add 4 ml of sulfuric acid (1+1) and 10 ml of hydrofluoric acid. Mix well with a platinum wire or the like, and heat carefully on a sand bath to dissolve. Continue volatilizing until the white fumes of sulfuric acid begin to be generated. After cooling, wash the inside walls with a small amount of water, and then add 1 ml of nitric acid and 5 ml of hydrofluoric acid. After mixing well, heat again on the sand bath to volatilize, and continue heating for 5 minutes after the white fumes of sulfuric acid begin to be generated. After cooling, wash the inside walls with a small amount of water, and heat again on the sand bath until dry. After cooling, transfer to a 250 ml volumetric flask, and bring up to volume with water.

### 14.1.2 Flame Atomic Absorption Method

**a) Target elements**

Al, Ca, Fe, K, Mg, Na, Ti

**b) Measurement procedures**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al**

**Reagents:**

Al standard solution (500 μg of Al/ml): Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Introduce an appropriate amount of pretreated sample (containing 0.5~10 mg of Al) into a 100 ml volumetric flask, and bring up to volume using hydrochloric acid (1+50). Use this solution for sample measurement. At this time, for a blank test, perform the same pretreatment on water as that used for the sample. Introduce the same volume of this

solution as that of the sample solution into a 100 ml volumetric flask, and bring up to volume using hydrochloric acid (1+50). The measurement value obtained with this solution is used for the correction value obtained with the actual sample.

2) For the calibration curve, place stepwise increments of 1~20 ml of the Al standard solution (500 μg of Al/ml) into 100 ml volumetric flasks. Add hydrochloric acid (1+50). to bring all the solutions up to volume.

**Measurement:**

Measurement wavelength: 309.3 nm

Calibration curve concentration range: 5~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 2)

Calculation is for aluminum oxide ($Al_2O_3$)

Multiply value obtained for Al by 1.89.

- **Ca**

**Reagents:**

1) Ca standard solution (10 μg of Ca/ml): Refer to Cookbook Section 2, item 3 Preparing Standards

2) La solution (50 g/l) : La solution (50 g/l) : Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent 2).

**Procedure:**

1) Place a suitable volume of pretreated sample (containing 5~150 μg of Ca) in a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water and use this solution for sample measurement. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample. Place the same volume of this solution in a 50 ml volumetric flask. Then, after adding 3 ml of La solution (50 g/l), bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.

2) For the calibration curve, place stepwise increments of 1~30 ml of the Ca standard solution (10 μg of Ca/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and add water to bring all the solutions up to volume. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 422.7 nm

Calibration curve concentration range: 0.2~6 μg/ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 9)

Calculation is for calcium oxide (CaO)

Multiply value obtained for Ca by 1.40.

- **Fe**

  **Reagents:**

  1) Fe standard solution (10 μg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

  **Procedure:**

  1) The pretreated sample may be directly used for measurement, or it may be diluted with hydrochloric acid (1+50) so that its concentration is within the quantitation range. At this time, take an appropriate amount of water and perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in sample measurement.
  2) For the calibration curve, introduce 3~60 ml of Fe standard solution (10 μg of Fe/ml) in stepwise volumes in 100 ml volumetric flasks. After adding acid using the same conditions as that for the sample, bring up to volume with water.

  **Measurement:**

  Measurement wavelength: 248.3 nm

  Calibration curve concentration range: 0.3~6 μg/ml

  Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16).

  Calculation is for diiron trioxide ($Fe_2O_3$)

  Multiply value obtained for Fe by 1.43.

- **Mg**

  **Reagents:**

  1) Mg standard solution (5 μg of Mg/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
  2) La solution (50 g/l) : Same as that described in item 12.1.2 Flame Atomic Absorption Method, •Ca reagent 2).

  **Procedure:**

  1) Introduce a suitable volume of pretreated sample (containing .2~2.5 μg of Mg) into a 50 ml volumetric flask. After adding 3 ml of La solution (50 g/l), bring up to volume with water for use in sample measurement. At this time, for a blank test, perform the same pretreatment on water as that performed for the sample. Place the same volume of this solution in a 50 ml volumetric flask. Then add 3 ml of La solution (50 g/l), and bring up to volume with water. The measurement value obtained with this solution is used for the correction value obtained with the actual sample.
  2) For the calibration curve, place stepwise increments of 0.5~5 ml of the Mg standard

solution (5 μg of Mg/ml) into 50 ml volumetric flasks. Add 3 ml of La solution (50 g/l) to each flask, and add water to bring all the solutions up to volume. Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 285.2 nm

Calibration curve concentration range: .0.05~0.5 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 22).

Calculation is for magnesium oxide (MgO)

Multiply value obtained for Mg by 1.66.

- **Ti**

**Reagents:**

1) Ti standard solution (500 μg of Ti/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Ammonium fluoride (50 g/l) : Same procedure as that described in item 13.2.2 Flame Atomic Absorption Method, •Ti, Reagent, 2).

**Procedure:**

1) Either use the pretreated sample directly, or dilute it with hydrochloric acid (1+50) so that its concentration is within the quantitation range. Add ammonium fluoride until its concentration reaches 2 g/l. This solution is used for measurement. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Add the same amount of ammonium fluoride (50 g/l) as that added to the sample, and then measure this solution. The obtained value may be used for the correction value obtained in the sample measurement.
2) For the calibration curve, place 1~20 ml of Ti standard solution (500 μg of Ti/ml) in stepwise volumes in 100 ml volumetric flasks. Add 4 ml of ammonium fluoride (50 g/l) and bring the solutions up to volume with hydrochloric acid (1+50). Use these solutions to generate the calibration curve.

**Measurement:**

Measurement wavelength: 364.3 nm

Calibration curve concentration range: 5~100 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 4).

Calculation is for titanium dioxide ($TiO_2$)

Multiply value obtained for Ti by 1.67.

- **K, Na**

**Reagents:**

1) Na standard solution (100 μg of Na/ml)

2) K standard solution (10 μg of K/ml)

For preparation of 1) and 2), refer to Cookbook Section 2, item 3 Preparing Standards.

3) Aluminum chloride solution : Dissolve 0.53 g of metallic aluminum in 10 ml of hydrochloric acid (1+1) and add water to bring up to 1000 ml.

4) Calcium chloride solution : Dissolve 0.56 g of calcium carbonate in 20 ml of hydrochloric acid (1+1) and add water to bring up to 1000 ml.

5) Magnesium chloride solution : Dissolve 0.60 g of metallic magnesium in 20 ml of hydrochloric acid (1+1) and add water to bring up to 1000 ml.

6) Standard mixed solutions: Standard solutions are prepared having concentrations of aluminum oxide, calcium oxide and magnesium oxide, which are near to those of the sample. Where the potassium oxide and sodium oxide concentrations are both greater and smaller than those of the sample, respectively are. Then, the aluminum oxide, calcium oxide and magnesium oxide are quantitated. After determining the approximate proportions of the potassium oxide and sodium oxide content, the solutions are prepared. For example, if the approximate mass percentages contained in the sample are NaO 14%, $K_2O$ 1%, $Al_2O_3$ 2%, CaO 8% and MgO 4%, 2 ml of aluminum chloride solution, 8 ml of calcium chloride solution, 4 ml of magnesium chloride solution and 1 ml of sulfuric acid (1+1) are introduced into a platinum dish and heated until dry. To this, 2 ml of hydrochloric acid (1+1) and about 30 ml of water are added and heated to dissolve. After cooling, the contents are transferred to a 100 ml volumetric flask, and brought up to volume with water. Introduce 5 ml of this solution into each of several 100 ml volumetric flasks. After adding 2~20 ml each, in stepwise increments, of Na standard solution (100 μg of Na/ml) and K standard solution (10 μg of K/ml), bring the solutions up to volume with water.

**Remark:** When determining the content percentages of potassium oxide and sodium oxide, prepare a standard mixed solution series containing no aluminum, calcium or magnesium, and having 0.2~2 mg Na/100 ml and 0.02~0.2 mg K/100 ml, and use these to generate the calibration curve.

**Procedure:**

1) Introduce 25 ml of sample solution into a 100 ml volumetric flask and bring up to volume with water. Then, accurately transfer 5 ml of this solution to a 100 ml volumetric flask. Add 2 ml of hydrochloric acid (1+1) and bring up to volume with water. Use this solution for sample measurement. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Dilute the same way as for the sample, and then measure this solution. The obtained value may

be used for the correction value obtained in the sample measurement.

2) Generate the calibration curve by measuring the standard mixed solutions.

**Measurement:**

**1) K**

Measurement wavelength: 766.5 nm

Calibration curve concentration range: 0.2~2 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 19).

**2) Na**

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 2~20 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 24).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

Calculation is for potassium oxide ($K_2O$)

Multiply value obtained for K by 1.20.

Calculation is for sodium oxide ($Na_2O$)

Multiply value obtained for Na by 1.35.

- **Ti**

**Reagents:**

1) Ti standard solution (100 μg of Ti/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

2) Ammonium fluoride (50 g/l) : Same procedure as described in item 13.2.2 Flame Atomic Absorption Method, •Ti, Reagent, 2)

**Procedure:**

1) Introduce a suitable amount of pretreated sample (containing 0.2~3 mg of Ti) into a 50 ml volumetric flask. Add 5 ml of ammonium fluoride (50 g/l), and bring up to volume with water. This solution is used for measurement. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Transfer to a 50 ml volumetric flask the same volume of this solution as that of the sample solution. After adding 5 ml of ammonium fluoride (50 g/l), bring up to volume with water, and perform measurement on this solution. The obtained value may be used for the correction value obtained in the sample measurement.

2) For the calibration curve, place 2~30 ml of Ti standard solution (100 μg of Ti/ml) in stepwise volumes in 50 ml volumetric flasks. Add 5 ml of ammonium fluoride (50 g/l) and bring the solutions up to volume with water. Use these solutions to generate the

calibration curve.

**Measurement:**

Measurement wavelength: 364.3 nm

Calibration curve concentration range: 10~70 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 41).

Calculation is for titanium dioxide ($TiO_2$)

Multiply value obtained for Ti by 1.67.

## 14.2 Boro-silicated Glass Analysis Method

**Reference materials:**

Japan Industrial Standards, Boro-silicated Glass Analysis Method, JIS R 3105

### 14.2.1 Sample Pretreatment

Same as described in item 14.1.1 Sample pretreatment

### 14.2.2 Flame Atomic Absorption Method

**a) Target elements**

Al, Fe, K, Na

**b) Measurement procedures**

Measurement is conducted using the following procedure. The lamp current value, slit width and flame conditions used are in accordance with Cookbook Section 3, item 6.4 Element Specific Measurement Conditions.

- **Al**

Same measurement procedure as that described in item 14.1.2 Flame Atomic Absorption Method of Al

- **Fe** (Standard Addition Method)

**Reagents:**

Fe standard solution (10 μg of Fe/ml) : Refer to Cookbook Section 2, item 3 Preparing Standards

**Procedure:**

1) Introduce appropriate amounts of pretreated Fe sample solution (containing 10~100 μg of Fe) into several 50 ml volumetric flasks. To one of the flasks add no Fe standard solution, and to the others add 5~25 ml of the Fe standard solution (10 μg of Fe/ml) in at least 3 incremental volumes. Then add hydrochloric acid (1+1) so that the acid concentration of each becomes 0.5 mol/l, and bring all the solutions up to volume with water. These solutions are used for measurement. For a blank test, pretreat the reagent using the same procedure as that used on the sample. Introduce this solution into a 50 ml volumetric flask in the same volume as the sample. Add hydrochloric acid so that the acid concentration becomes 0.5 mol/l, and use this solution for the blank sample measurement.
2) Generate a calibration curve using the signals from the measurement of the solutions of

step 1). After verifying its linearity, use this to extrapolate the Fe concentrations in the samples.

**Measurement:**

Measurement wavelength: 248.3 nm

Calibration curve concentration range: 0.2~5 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 16)

Calculation is for diiron trioxide ($Fe_2O_3$)

Multiply value obtained for Fe by 1.43.

- **K, Na**

**Reagents:**

1) K standard solution (200 μg of K/ml)
2) Na standard solution (10 μg of Na/ml)

   For preparation of 1) and 2), refer to Cookbook Section 2, item 3 Preparing Standards.
3) Aluminum chloride solution : Same procedure as described in item 1.4.12 Flame Atomic Absorption Method, •K, Na, Reagent, 3)
4) Standard mixed solutions : Standard solutions are prepared in which the concentration of aluminum oxide is near to that of the sample, and where the sodium oxide and potassium oxide concentrations are both greater and smaller than those of the sample, respectively are. For example, if the approximate mass percentage content of $Al_2O_3$ is 2.0%, introduce 5 ml of aluminum chloride solution and 2 ml of sulfuric acid (1+1) into a platinum dish, and heat until dry. To this, add 2 ml of hydrochloric acid (1+1) and about 30 ml of water and heat to dissolve. After cooling, transfer to a 250 ml volumetric flask, and bring up to volume with water. Introduce 5 ml of this solution into each of several 100 ml volumetric flasks. After adding 2~20 ml each, in stepwise increments, of Na standard solution (200 mg of Na/ml) and K standard solution (10 mg of K/ml), bring the solutions up to volume with water.

**Procedure:**

1) Introduce 25 ml of sample solution into a 100 ml volumetric flask and bring up to volume with water for the measurement of K. For measurement of Na, introduce 10 ml of this solution to a 100 ml volumetric flask. Add 2 ml of hydrochloric acid (1+1) and bring up to volume with water. At this time, for a blank test, take an appropriate amount of water and perform the same pretreatment as that used for the sample. Dilute the same way as for the sample, and then measure this solution. The obtained value may be used for the correction value obtained in the sample measurement.
2) For the calibration curve, the standard mixed solutions may be used with respect to the

K concentration. For Na, transfer 10 ml of the mixed standard solutions to 100 ml volumetric flasks. Add 2 ml of hydrochloric acid (1+1), and bring up to volume with water. Use these solutions to generate the calibration curve.

**Measurement:**

**1) K**

Measurement wavelength: 766.5 nm

Calibration curve concentration range: 0.2~2 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 19).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

**2) Na**

Measurement wavelength: 589.0 nm

Calibration curve concentration range: 0.4~4 μg/ml

Measurement conditions: Refer to Cookbook Section 3, item 6.4, 24).

**Remark:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

Calculation is for potassium oxide ($K_2O$)

Multiply value obtained for K by 1.20.

Calculation is for sodium oxide ($Na_2O$)

Multiply value obtained for Na by 1.35.

# Atomic Absorption Analysis Cookbook

## Section 8

## Non-ferrous Metals Analysis

SHIMADZU CORPORATION
KYOTO, JAPAN

Atomic Absorption Analysis Cookbook

Section 8

# Table of Contents

## Introduction

Cookbook Section 8 describes the methods used for analysis of non-ferrous metals.

These analysis methods, detailed in the Japan Industrial Standards, are for elements to be analyzed by the atomic absorption method. They were modified to provide the optimum results when using a Shimadzu atomic absorption spectrophotometer.

These analysis methods assume that the sample compositions conform to Japan Industrial Standards specifications, but for cases in which the actual sample compositions differ from the Japan Industrial Standards, the pretreatment method, interference at time of measurement, background absorption and flame conditions may not necessarily apply.

The measurement conditions provided here are appropriate when using an AA-6000 Series Atomic Absorption Spectrophotometer. When using another atomic absorption spectrophotometer, the calibration curve concentration range and measurement conditions must be corrected.

# 15. Non-ferrous Metals Analysis

## 15.1 Copper and Copper Alloy Analysis Method

Reference materials:

Japan Industrial Standard, Copper and Copper Alloy Atomic Absorption Analysis Method, JIS H 1291

### 15.1.1 Sample Pretreatment

Weigh out 1.0g of sample to the nearest 1mg, transfer it to a 200m*l* beaker, and cover with a watch glass. After adding 20m*l* of an acid mixture containing 1 part hydrochloric acid, 1 part nitric acid, and 2 parts water, heat gently to decompose. Rinse the bottom of the watch glass ,and the inner wall of the beaker with about 10m*l* of water, and heat gently to drive off the nitric acid compounds. After cooling, rinse into a 100m*l* volumetric flask, and dilute to bring up volume.

**Note:** For silicon, pitch copper bronze, weigh out 1.0g of sample into a 100m*l* polyethylene beaker. After decomposing with 20m*l* of the acid mixture, add 5m*l* of hydrofluoric acid (1+9) and mix. Then add 10m*l* of boric acid solution (5 w/v%) and heat for about 15minutes at 70 – 80°C. After cooling, rinse with water into a 10m*l* volumetric flask, and dilute to bring up to volume.

### 15.1.2 Flame Atomic Absorption Method

**a) Target element and quantitation range**

| Element | Percent Contained (%) |
|---|---|
| Al | 0.1 – 3.0 |
| Be | 0.2 – 2.0 |
| Co | 0.01 – 1.0 |
| Cr | 0.01 – 2.0 |
| Fe | 0.01 – 6.0 |
| Mn | 0.01 – 3.0 |
| Ni | 0.01 – 7.0 |
| Pb | 0.01 – 4.5 |
| Si | 0.1 – 4.0 |
| Sn | 0.02 – 4.0 |
| Zn | 0.01 – 1.0 |

**b) Measurement procedures**

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

**Reagents:**

1) Al standard solution (1000µg Al/m*l*)
2) Be standard solution (1000µg Be/m*l*)
3) Co standard solution (1000µg Co/m*l*)
4) Cr standard solution (1000µg Cr/m*l*)
5) Fe standard solution (1000µg Fe/m*l*)
6) Mn standard solution (1000µg Mn/m*l*)
7) Ni standard solution (1000µg Ni/m*l*)
8) Pb standard solution (1000µg Pb/m*l*)
9) Si standard solution (1000µg Si/m*l*)
10) Sn standard solution (1000µg Sn/m*l*)
11) Zn standard solution (1000µg Zn/m*l*)

For 1) – 11) above, refer to Cookbook Section 2, Item 3 Preparing Standard.

**Procedure:**

1) Depending on the percent of quantitation element contained, use the apportion ratio of the following table to introduce the appropriate aliquot of pretreated solution into 100m*l* volumetric flask, and bring up to volume with hydrochloric acid (1+9).

   At this time, for a blank test, take an appropriate amount of reagent containing no sample, and perform the same pretreatment as that used for the sample. Use this solution to determine the amount of target element contained using a calibration curve generated for the blank test. The obtained value may be used for correction of the value obtained in sample measurement.

**Note:** To generate the calibration curve for the blank test, add increasing concentrations of the target element to several volumetric flasks containing 20m*l* of the acid mixture, and then dilute with water to bring up to volume.

**Apportion Ratio Example**

| Element | Percent Contained (%) | Apportion Ratio | Concentration Range (µg/100m*l*) |
|---|---|---|---|
| Al | 0.1 – 3.0 | 1/5 | 0.2 – 6.0 |
| Be | 0.1 – 2.0 | 1/10 | 0.1 – 0.2 |
| Co | 0.01 – 0.2<br>0.1 – 1.0 | 1/5<br>1/20 | 0.02 – 0.4<br>0.05 – 0.5 |
| Cr | 0.01 – 0.2 | 1/5 | 0.02 – 0.4 |
| Fe | 0.01 – 0.2<br>0.1 – 2.0<br>1.0 – 6.0 | 1<br>1/10<br>1/20 | 0.1 – 2.0<br>0.1 – 2.0<br>0.5 – 3.0 |

| | | | |
|---|---|---|---|
| Mn | 0.1 – 0.1 | 1 | 0.1 – 1.0 |
| | 0.1 – 1.0 | 1/10 | 0.1 – 1.0 |
| | 0.5 – 3.0 | 1/20 | 0.25 – 1.5 |
| Ni | 0.01 – 0.2 | 1 | 0.1 – 2.0 |
| | 0.2 – 2.0 | 1/10 | 0.2 – 2.0 |
| | 1.0 – 7.0 | 1/20 | 0.5 – 3.5 |
| Pb | 0.01 – 0.2 | 1 | 0.1 – 2.0 |
| | 0.2 – 2.0 | 1/10 | 0.2 – 2.0 |
| | 1.0 – 4.5 | 1/20 | 0.5 – 2.5 |
| Si | 0.1 – 1.0 | 1 | 1.0 – 10 |
| | 0.5 – 4.0 | 1/5 | 1.0 – 8.0 |
| Sn | 0.02 – 1.0 | 1 | 0.2 – 10 |
| | 1.0 – 4.0 | 1/5 | 2.0 – 8.0 |
| Zn | 0.01 – 0.1 | 1/5 | 0.02 – 0.2 |
| | 0.1 – 0.5 | 1/10 | 0.1 – 0.5 |
| | 0.5 – 1.0 | 1/20 | 0.5 – 1.0 |

2) When generating the calibration curve, prepare a standard solution having as similar composition as possible of copper and the other main constituents as in the sample solution, and introduce increasing concentrations of the copper solution with its other constituents into several 100m*l* volumetric flasks. To each, add increments of the standard solution for each element. Then add hydrochloric acid (1+1) so that its concentration is approximately the same as that in the sample solution. Dilute with water to bring up to volume.

**Note:** The main constituent in the alloy varies with the type of alloy. Normally, it is a good idea to target many elements. For example, brass contains copper and zinc/phosphorous, bronze contains copper and tin/special aluminum, bronze contains copper, aluminum, iron, manganese and nickel/ German silver contains copper, zinc and nickel.

## Example of Standard Solution Addition Amount

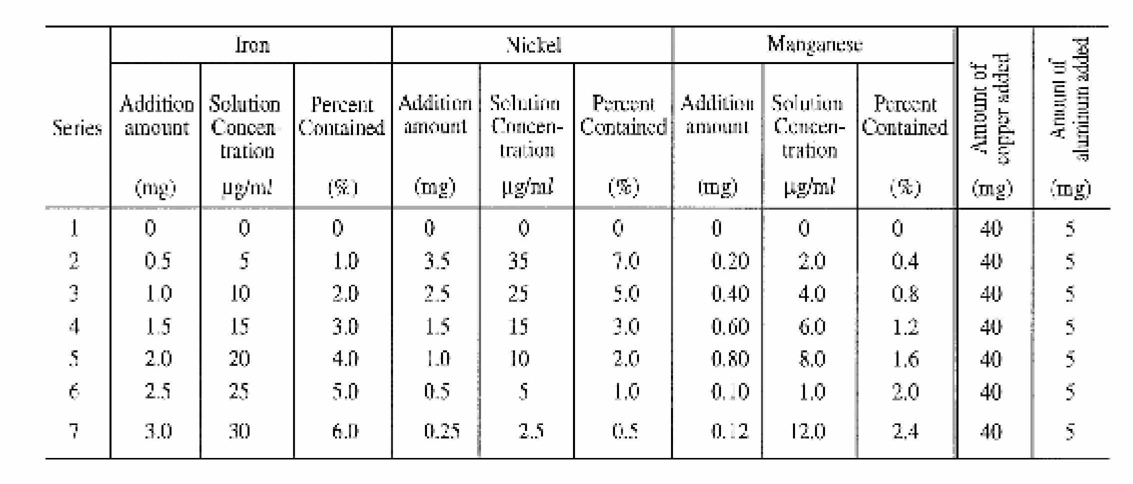
1) Brass (copper) containing 59.0 – 62.0% lead and iron (Use apportion ratio 1)

Liquid quantity: 100m*l*

| Series | Lead and Iron Addition Amount (mg) | Solution Concentration (µg/m*l*) | Percent Contained (%) | Amount of copper added (mg) | Amount of lead added (mg) |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 600 | 400 |
| 2 | 0.10 | 1.0 | 0.01 | 600 | 400 |
| 3 | 0.30 | 3.0 | 0.03 | 600 | 400 |
| 4 | 0.60 | 6.0 | 0.06 | 600 | 400 |
| 5 | 0.90 | 9.0 | 0.09 | 600 | 400 |
| 6 | 1.2 | 12.0 | 0.12 | 600 | 400 |

2) Example showing iron, nickel and manganese in special aluminum (Use apportion ratio 1/20)

Liquid quantity: 100ml



| Series | Iron | | | Nickel | | | Manganese | | | Amount of copper added | Amount of aluminum added |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Addition amount (mg) | Solution Concentration µg/ml | Percent Contained (%) | Addition amount (mg) | Solution Concentration µg/ml | Percent Contained (%) | Addition amount (mg) | Solution Concentration µg/ml | Percent Contained (%) | (mg) | (mg) |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 40 | 5 |
| 2 | 0.5 | 5 | 1.0 | 3.5 | 35 | 7.0 | 0.20 | 2.0 | 0.4 | 40 | 5 |
| 3 | 1.0 | 10 | 2.0 | 2.5 | 25 | 5.0 | 0.40 | 4.0 | 0.8 | 40 | 5 |
| 4 | 1.5 | 15 | 3.0 | 1.5 | 15 | 3.0 | 0.60 | 6.0 | 1.2 | 40 | 5 |
| 5 | 2.0 | 20 | 4.0 | 1.0 | 10 | 2.0 | 0.80 | 8.0 | 1.6 | 40 | 5 |
| 6 | 2.5 | 25 | 5.0 | 0.5 | 5 | 1.0 | 0.10 | 1.0 | 2.0 | 40 | 5 |
| 7 | 3.0 | 30 | 6.0 | 0.25 | 2.5 | 0.5 | 0.12 | 12.0 | 2.4 | 40 | 5 |

**Measurement:**

1) **Al**

Wavelength : 309.3nm

Calibration curve range : 2 – 60µg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 2

2) **Be**

Wavelength : 234.9nm

Calibration curve range : 0.2 – 2µg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 7

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

3) **Co**

Wavelength : 240.7nm

Calibration curve range : 0.2 – 5µg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 12

4) **Cr**

Wavelength : 357.9nm

Calibration curve range : 0.2 – 5µg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 13

**5) Fe**

Wavelength : 248.3nm

Calibration curve range : 0.2 – 5μg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 16

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

**6) Mn**

Wavelength : 279.5nm

Calibration curve range : 0.2 – 5μg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 22

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

7) Ni

Wavelength : 232.0nm

Calibration curve range : 0.2 – 5μg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 26

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

**8) Pb**

Wavelength : 283.3nm

Calibration curve range : 1 – 20μg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 27

**9) Si**

Wavelength : 251.6nm

Calibration curve range : 10 – 200μg /ml

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 34

**10) Sn-1**

Wavelength : 224.6nm

Calibration curve range : 5 – 100μg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 37

Sn-2

Wavelength : 224.6nm

Calibration curve range : 10 – 200μg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 35

Sn-3

Wavelength : 286.3nm

Calibration curve range : 20 – 300μg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 36

**11) Zn**

Wavelength : 213.9nm

Calibration curve range : 0.05 – 1μg /m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 44

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

## 15.2 Analysis Method for Oxygen Free Copper for Electron Tubes

**Reference materials:**

Japan Industrial Standard Analysis Method for Oxygen Free Copper for Electron Tubes, JIS H 1202

### 15.2.1 Sample Pretreatment

**a) Bi** (Tri-n-octylmethylammonium bromide extraction)

Weigh out 5.0g of sample to the nearest 10mg. Transfer to a 200m*l* beaker, cover with a watch glass, and add 30m*l* of nitric acid (1+1) and heat gently to decompose. Rinse the watch glass and the inner wall of the beaker with a small amount of water. Continue to heat to concentrate, and then heat on a water bath to volatilize until evaporated. To this, add 2m*l* of nitric acid (1+1) and 10m*l* of water. Heat to dissolve the salts, and add water to bring the volume to about 50m*l*.

To this solution, accurately add 7.5ml of hydrobromic acid (1+8), add water to bring volume to about 80m*l*. Using a pH meter, add sodium hydroxide solution to adjust the pH to 1.5 – 1.7. Then transfer to a 200m*l* separating funnel and add water to bring volume to 150m*l*. Add exactly 10m*l* of extraction solvent, and after shaking vigorously for about 5 minutes, let stand until contents separate into 2 layers. Then remove the aqueous phase. Pass the organic phase through dry filter paper or degreased cotton. Transfer to a 15 – 20m*l* stoppered test tube, and add butyl acetate to bring volume to 10m*l*.

**Note:** Extraction solvent: Add butyl acetate to 6ml of tri-n-octylmethylammonium chloride to bring to a volume of 40ml. Transfer this solution to a 100ml separating funnel, add 40ml of hydrobromic acid (1+8). After shaking vigorously, remove the aqueous phase and dilute the organic phase with butyl acetate by a factor of 5.

**b)** **Cd, Zn** (Tri-n-octylamine extraction)

Weigh out 2.0g of sample to the nearest 10mg, and transfer to a quartz beaker. Cover with a watch glass, add 10m*l* of nitric acid(1+1), and heat gently to decompose. Rinse the watch glass and the inner wall of the beaker with a small amount of water, add 20m*l* of sulfuric acid (1+1), and continue heating until the white fumes of sulfuric acid are generated to remove the nitric acid. After cooling, add 40m*l* of hydrochloric acid (1+1) to dissolve the salts, transfer to a 200m*l* separating funnel, and add water to bring volume to 100m*l*. Add 5m*l* of extraction solvent, and after shaking vigorously, let stand until contents separate into 2 layers. Then transfer the aqueous phase to a 200m*l* separating funnel.

To this, add 5m*l* of extraction solvent, and after shaking vigorously for about 5 minutes, let stand until contents separate into 2 layers. Then remove the aqueous phase. Pass the organic phase through dry filter paper or degreased cotton, transfer both to a 15 – 25m*l* stoppered test tube, and add 4-methyl-2-pentanone (MIBK) to bring volume to 15m*l*.

Note: Extraction solvent: Dissolve 2m*l* of tri-n-octylamine and dilute to 100m*l*.

**c)** **Pb** (Tri-n-octylmethylammonium bromide extraction)

Weigh out 3.0g of sample to the nearest 10mg, transfer to a 200m*l* beaker, cover with a watch glass, add 10m*l* of nitric acid (1+1) and heat gently to decompose. Rinse the watch glass and the inner wall of the beaker with a small amount of water, add 40m*l* of sulfuric acid (1+1), and continue heating until the white fumes of sulfuric acid are generated to completely drive off the nitric acid.

After cooling, add 70m*l* of water, then add exactly 30m*l* of hydrobromic acid (1+8), and gently heat to dissolve the salts. After cooling, transfer to a 200m*l* separating funnel, and add water to bring volume to 150m*l*. Add exactly 10m*l* of extraction solvent, and after shaking vigorously for about 5 minutes, let stand until contents separate into 2 layers. Then remove the aqueous phase. Pass the organic phase through dry filter paper or degreased cotton, transfer to a 15 – 20m*l* stoppered test tube, and add butyl acetate to bring volume to 10m*l*.

**Note:** Extraction solvent: Same procedure as that for Bi (Tri-n-octyl-methyl-ammonium bromide extraction)

**d)** **Pb** (Iron hydroxide precipitation separation)

Weigh out 20g of sample to the nearest 10mg, transfer to a 500m*l* beaker, cover with a watch glass. After adding 160m*l* of nitric acid to decompose, boil gently to drive off the nitrogen oxide. Then add water to bring up to 300m*l*. Add 5m*l* of ferric ammonium sulfate (10 w/v%), and while mixing, add aqueous ammonia to dissolve the copper hydroxide precipitate.

After it dissolves, add 50m*l* more. Next, add 15g of ammonium carbonate and heat. After boiling gently for about 5 minutes, set aside in a warm location (60 – 80°C) for 1 – 2 hours.

Separate the precipitate using Type 5A filter paper, and after rinsing several times with warm ammonia, rinse solution (made by adding 15g of ammonium carbonate to 500m*l* of ammonia (2+50)), transfer it to the original beaker by rinsing with warm water. Place the beaker under the filter, and drip 10m*l* of hydrochloric acid over the filter paper to dissolve the precipitate on the filter paper and in the beaker. Rinse the filter paper with warm hydrochloric acid (1+50).

Heat the combined filtrate and rinse solution in the beaker to concentrate it. After its volume is decreased to about 10m*l*, transfer it to a 100m*l* beaker using hydrochloric acid (1+50). Add 2m*l* of sulfuric acid (1+1) and heat the concentrate to dryness. After cooling, add 8m*l* of hydrochloric acid (1+1), heat to dissolve. After cooling, transfer to a 25m*l* volumetric flask using hydrochloric acid (1+50), and dilute up to volume.

### 15.2.2 Flame Atomic Absorption Method

#### a) Target element and quantitation range

| | | |
|---|---|---|
| Bi | Tri-n-octylmethylammonium bromide extraction | 0.00002% |
| Cd | Tri-n-octylamine extraction | 0.00002% |
| Pb | Tri-n-octylmethylammonium bromide extraction | 0.00005% |
| | Iron hydroxide precipitation separation | 0.0001% |
| Zn | Tri-n-octylamine extraction | 0.00002% |

#### b) Measurement procedures

Measurement is conducted using the following procedure. To generate the calibration curve, refer to Cookbook Section 2, Item 3 Preparing Standards.

- **Bi**

**Reagent:**

Bi standard solution (100µg of Bi/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

**Procedure:**

1) The sample solution pretreated according to section a) above can be used for measurement as it is. At this time, take an appropriate amount of reagent containing no sample, perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.
2) For the standard solutions used to generate the calibration curve, take several aliquots of Bi standard solution (100µg of Bi/m*l*) with increasing concentrations of Bi from 0 – 50µg, and to each of these, add exactly 30m*l* of sodium nitrate solution (8.5 w/v%) and 7.5m*l* of hydrobromic acid (1+8). Transfer these solutions to 200m*l* separating funnels, add water to bring each of the volumes to 150m*l*. Add the extraction solvent used in the

sample pretreatment and conduct measurement using to the following conditions.

**Measurement:**

Measurement wavelength : 223.3nm

Calibration curve range : 0.5 – 5µg /m*l*

Measurement conditions :

Lamp current : 10mA

Slit width : 0.5nm

Lamp mode : BGC-$D_2$

Burner height : 7mm

Support gas : Air

Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- **Cd**

**Reagent:**

Cd standard solution (100µg of Cd/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

**Procedure:**

1) The sample solution pretreated according to section b) is processed in the same way as that described in Procedure 1) for Bi.
2) For the standard solutions used to generate the calibration curve, take several aliquots of Cd standard solution (100µg of Cd/m*l*) with increasing concentration of Cd from 0 – 6µg, and to each of these, accurately add 20m*l* of sulfuric acid (1+1) and 40m*l* of hydrochloric acid (1+1). Transfer these solutions to 200m*l* separating funnels, add water to bring each of the volumes to 150m*l*, add the extraction solvent used in the sample pretreatment and conduct measurement using the following conditions.

**Measurement:**

Measurement wavelength : 228.8nm

Calibration curve range : 0.05 – 0.4µg /m*l*

Measurement conditions :

Lamp current : 8mA

Slit width : 0.5nm

Lamp mode : BGC-$D_2$

Burner height : 7mm

Support gas : Air

Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- Pb I (Tri-n-octylmethylammonium bromide extraction)

  **Reagent:**

  Pb standard solution (100µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

  **Procedure:**

  1) The sample solution pretreated according to section c) is processed in the same way as that described in Procedure 1) for Bi.
  2) For the standard solutions used to generate the calibration curve, take several aliquots of Bi standard solution (100µg of Pb/m*l*) with increasing concentrations of Pb from 0 – 50µg, and to each of these, accurately add 15m*l* of sulfuric acid (1+1) and 30m*l* of hydrobromic acid (1+8). Transfer these solutions to 200m*l* separating funnels. Add water to bring each of the volumes to 150m*l*, add the extraction solvent used in the sample pretreatment and conduct measurement using the following conditions.

  **Measurement:**

  Measurement wavelength : 217.0nm
  Calibration curve range : 0.5 – 5µg /m*l*
  Measurement conditions :
    Lamp current : 12mA
    Slit width : 0.5nm
    Lamp mode : BGC-$D_2$
    Burner height : 7mm
    Support gas : Air
    Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- **Pb II** (Iron hydroxide precipitation separation)

  **Reagent:**

  Pb standard solution (100µg of Pb/m*l*): Same as for Pb I Procedure:

  **Procedure:**

  1) The sample solution pretreated according to section d) is processed in the same way as that described in Procedure 1) for Bi.
  2) For the standard solutions used to generate the calibration curve, transfer to 100m*l* beakers several aliquots of Pb standard solution (100µg of Pb/m*l*) with increasing concentrations of Pb from 0 – 200µg. To each of these, accurately add 5m*l* of ferric ammonium sulfate (10 w/v%) and 2m*l* of sulfuric acid (1+1). Heat until evaporated, add

10m*l* of hydrochloric acid (1+1), and use this for measurement.

**Measurement:**

Measurement wavelength : 283.3nm

Calibration curve range : 1 – 10μg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

- **Zn**

**Reagent:**

Zn standard solution (100μg of Zn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

**Procedure:**

1) The sample solution pretreated according to section b) is processed in the same way as that described in Procedure 1) for Bi.
2) For the standard solutions used to generate the calibration curve, follow the same procedure as that for Cd, using the Zn standard solution (100μg of Zn/m*l*) and the range of 0 – 3μg of Zn.

Measurement:

Measurement wavelength : 213.9nm

Calibration curve range : 0.05 – 0.3μg /m*l*

Measurement conditions :

Lamp current : 8mA

Slit width : 0.5nm

Lamp mode : BGC-$D_2$

Burner height : 7mm

Support gas : Air

Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

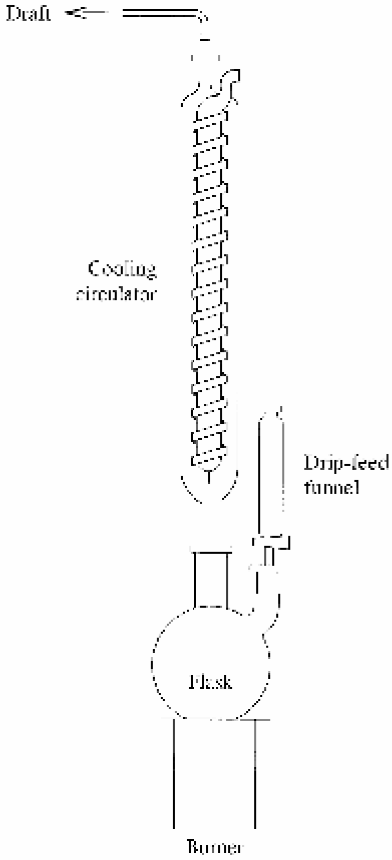
### 15.2.3 Reduction Vaporization Atomic Absorption Method

#### a) Target Element and quantitation range

Hg 0.00001% or higher

#### b) Sample pretreatment

Weigh out 3g of sample to the nearest 10mg and transfer to a 250 – 300m*l* decomposition flask, as shown in the figure at under. Attach the cooling circulator and drip-feed funnel. Add 20m*l* of acid mixture (sulfuric acid 3 parts + nitric acid 1 part + water 6 parts), and heat gently to decompose. After cooling, add 10m*l* of urea solution (5 w/v%), and boil for about 5 minutes. After allowing to cool a little, add about 30m*l* of water and add 5m*l* of potassium permanganate solution (5 w/v%), and boil for 20 minutes. After cooling, rinse the cooling circulator and drip-feed funnel with water. To this solution, drip-feed hydroxyl ammonium hydrochloride (20 w/v%). When the red color disappears due the permanganate ion, transfer to a 300m*l* reducing flask using water, and further dilute to bring up to 200m*l*.



**Decomposition Flask with Cooling Circulator**

### c ) Measurement procedure

**Reagents:**

1) Hg standard solution (0.1μg Hg/m*l*) : Refer to Cookbook Section 2, item 3 Preparing Standards
2) Stannous chloride solution (10 w/v%) : Add 10g of stannous chloride to 60m*l* of sulfuric acid (sulfuric acid to water ratio 1:20), and while heating, mix to dissolve. After cooling, bring up to 100m*l* using water.

**Procedure:**

1) The pretreated sample may be measured as it is.
2) For the calibration curve, prepare standard solutions starting with incremental volumes between 2.0 – 10.0m*l* of the Hg standard solution (0.1μg Hg/m*l*). To each, add 5m*l* of

sulfuric acid (1+1), and bring up to 200m*l* using water.

**Measurement:**

Connect the MVU-1A Mercury Vaporizer Unit to the atomic absorption spectrophotometer, and measure the sample. For details on operation of the MVU-1A, refer to its accompanying documentation.

Measurement wavelength : 253.7nm
Calibration curve range : 1 – 5 ng/m*l*
Measurement conditions :
  Lamp current : 4mA
  Slit width : 0.5nm
  Lamp mode : BGC-$D_2$

## 15.3 Electrolytic Copper Ore Analysis Method

**Reference materials:**

Japan Industrial Standard, Electrolytic Copper Ore Analysis Method JIS H 1291

### 15.3.1 Sample Pretreatment

**a) As, Bi, Pb, Sb**

1) Weigh out 10g of sample to the nearest 10mg and transfer to a 500m*l* beaker. Cover with a watch glass, add 80m*l* of nitric acid (1+1) to decompose, and boil gently to drive off the nitrogen oxide. After cooling to ambient temperature, rinse the bottom surface of the watch glass with water and remove the watch glass. Then add water to bring to a final volume of 200m*l*.

2) Add 4m*l* of iron (III) solution and 4m*l* of lanthanum nitrate, and while mixing this solution, add aqueous ammonia until the copper hydroxide precipitate dissolves. Then add 50m*l* more. Heat this solution and boil gently for 5 minutes. Filter out the precipitate using Type 5B filter paper, and rinse several times using warm ammonium rinse solution. Discard the rinse liquid and filtrate.

3) Using warm water, rinse the precipitate on the filter paper back into the original beaker, place the beaker under the funnel. Drip 10m*l* of a nitric acid mixture onto the filter paper to dissolve any remaining precipitate. Heat both the filtrate and rinse solution until the precipitate is completely dissolved and keep heating until the hydrogen peroxide is driven off. After cooling to ambient temperature, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water.

**Note:**

1) Iron (III) solution: Add 20m*l* of nitric acid mixture to 0.5g of iron (99.9%), and after heating to dissolve, keep heating until hydrogen peroxide is driven off. After cooling to ambient temperature, dilute to 100m*l* using water (Fe 5μg/m*l*).

2) Lanthanum nitrate solution: Dissolve 1.6g of lanthanum nitrate 6-hydrate in 100m*l* of nitric acid (1+100) (La 5μg/m*l*).

3) Nitric acid mixture: Add 10m*l* of hydrogen peroxide to 100m*l* of nitric acid (1+1) (Prepare

each time).

4) Ammonia rinse solution: Dissolve 15g of ammonium carbonate in 500m*l* of aqueous ammonia (2+50).

5) If there is more than 4µg of As, Bi, Pb and Sb in the sample, after completing step 1) of the above procedure, us a portion containing 2 – 4µg for steps 2) and thereafter.

**b) Bi, Pb, Sb** (Flame Atomic Absorption Method)

1) Weigh out 20g of sample to the nearest 10mg and transfer to a 500m*l* beaker. Cover with a watch glass, add 160m*l* of nitric acid to dissolve. Heat and boil gently to drive off the nitrogen oxide. After cooling to ambient temperature, rinse the bottom of the watch glass with water, remove the watch glass, and add water to bring volume to about 200m*l*.

2) Add 4m*l* of iron (III) solution and 4m*l* of lanthanum nitrate. While mixing this solution, add aqueous ammonia until the copper hydroxide precipitate dissolves, and then add 50m*l* more. Heat this solution and boil gently for 5 minutes. Filter out the precipitate using Type 5B filter paper, and rinse several times using warm ammonium rinse solution. Discard the rinse liquid and filtrate.

3) Using warm water, rinse the precipitate on the filter paper back into the original beaker, place the beaker under the funnel, and drip 10m*l* of a nitric acid mixture onto the filter paper to dissolve any remaining precipitate. Heat both the filtrate and rinse solution until the precipitate is completely dissolved. Transfer to a 200m*l* beaker using a small amount of water, and heat this solution to concentrate it down to a volume of about 10m*l*. After cooling to ambient temperature, transfer to a 25m*l* volumetric flask using water, and bring up to volume with water.

**Note:**

1) Iron (III) solution
2) Lanthanum nitrate solution
3) Nitric acid mixture
4) Ammonia rinse solution

Preparation of 1) – 4) above is the same as described in a) Notes 1) – 4).

5) If there is more than 250µg of Bi, Pb and Sb in the sample, transfer from the 25m*l* flask of step 3) a volume providing 50 – 250µg of the elements to another 25m*l* volumetric flask. Add 4m*l* of the iron (III) solution, 4m*l* of the lanthanum nitrate and 5m*l* of nitric acid (1+1), and bring up to volume with water.

**c) Fe** (Flame Atomic Absorption Method)

1) Weigh out 20g of sample to the nearest 10mg and transfer to a 500m*l* beaker. Cover with a watch glass, add 160m*l* of nitric acid to dissolve. Heat and boil gently to drive off the nitrogen oxide. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass, transfer to a 200m*l* volumetric flask using water, and bring up to volume with water.

2) Transfer exactly 50m*l* of this solution to a beaker (If there is a large amount of Fe contained in the sample, decrease the volume so that 10 – 50μg of Fe is transferred). Heat until the solution is concentrated to a syrupy consistency. After allowing to cool, add 20m*l* of hydrochloric acid (1+1), heat gently to dissolve the salts, and cool to ambient temperature. Transfer to a 100m*l* separating funnel using hydrochloric acid (1+1), and add hydrochloric acid (1+1) to bring up to a volume of 50m*l*. Add 20m*l* of 4-methyl-2-pentanone isopentyl acetate solvent mixture, and shake vigorously. After allowing it to separate into 2 layers, discard the aqueous layer. Repeat this procedure once more.

3) Add about 20m*l* of water to the organic phase, shake vigorously for about 1 minute, and after allowing it to separate into 2 layers, transfer the aqueous phase to a 50m*l* beaker. Once again, add 5m*l* of water to the organic phase, shake vigorously for about 1 minute, and after allowing it to separate into 2 layers, combine the aqueous phase with the previous portion in the 50m*l* beaker. Add 5m*l* of sulfuric acid (1+1) to this solution, and heat until evaporated. After allowing to cool, add 5m*l* of hydrochloric acid (1+1), and heat to dissolve the salts. After cooling to ambient temperature, transfer to a 25m*l* volumetric flask using water, and bring up to volume.

Note: 4-methyl-2-pentanone isopentyl acetate solvent mixture: Mix 1 part 4-methyl-2-pentanone with 1 part isopentyl acetate.

### 15.3.2 Electrical Heating Atomic Absorption Method

**a) Target element and quantitation range**

| Element | Percent contained (%) |
|---|---|
| As | 0.00005 – 0.005 |
| Bi | 0.00005 – 0.005 |
| Pb | 0.00005 – 0.005 |
| Sb | 0.00005 – 0.005 |

**b) Measurement procedure**

Measurement is conducted using the following procedure. For the lamp current and slit width, refer to Cookbook Section 4, Item 7.5 Element Specific Measurement Conditions.

- **As (Iron hydroxide - lanthanum hydroxide precipitation separation)**

  **Reagents:**

  1) As standard solution (1μg of As/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.

2) Iron (III) solution
3) Lanthanum nitrate solution

Preparation of 2), 3) above is the same as described in a) Note 1), 2).

**Procedures**:

1) The sample solution pretreated according to step a) is measured just as it is. For blank measurement, perform the same pretreatment procedure on the reagent containing no sample, measure this solution, and use the value obtained to correct the value obtained in sample measurement.
2) For the standard solutions to be used for generating the calibration curve, transfer both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to several 100m*l* volumetric flasks, and add increasing volumes of the As standard solution (1µg of As/m*l*) from 0 – 4.0m*l* (As content from 0 – 4µg). After adding 10m*l* of nitric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

Measurement wavelength : 193.7nm
Calibration curve range : 2 – 40 ng/m*l*
Tube : High density graphite tube
Sample injection volume : 20µ*l*
Heating conditions:

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 10 | R | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- Bi (Iron hydroxide - lanthanum hydroxide precipitation separation)

Reagents:

1) Bi standard solution (1µg of Bi/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution

3) Lanthanum nitrate solution

Preparation of 2), 3) above is the same as described in a) Note 1), 2).

**Procedures:**

1) Sample measurement is the same as that described for As Procedures 1).
2) For the standard solutions to be used for generating the calibration curve, transfer both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to several 100m*l* volumetric flasks, and add increasing volumes of the Bi standard solution (1μg of Bi/m*l*) from 0 – 4.0m*l* (Bi content from 0 – 4μg). After adding 10m*l* of nitric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

| | |
|---|---|
| Measurement wavelength | : 223.1nm |
| Calibration curve range | : 2 – 40 ng/m*l* |
| Tube | : High density graphite tube |
| Sample injection volume | : 20μ*l* |

Heating conditions:

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- **Pb (Iron hydroxide -** lanthanum hydroxide precipitation separation)

**Reagents:**

1) Pb standard solution (1μg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution
3) Lanthanum nitrate solution

Preparation of 2), 3) above is the same as described in a) Note 1), 2).

**Procedures:**

1) Sample measurement is the same as that described for As Procedures 1).

2) For the standard solutions to be used for generating the calibration curve, transfer both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to several 100m*l* volumetric flasks, and add increasing volumes of the Pb standard solution (1µg of Pb/m*l*) from 0 – 4.0m*l* (Pb content from 0 – 4µg). After adding 10m*l* of nitric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

Measurement wavelength : 283.3nm
Calibration curve range : 2 – 40 ng/m*l*
Tube : High density graphite tube
Sample injection volume : 20µ*l*
Heating conditions:

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- Sb (Iron hydroxide - lanthanum hydroxide precipitation separation)

**Reagents:**

1) Sb standard solution (1µg of Sb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution
3) Lanthanum nitrate solution
4) Nitric acid mixture
5) Ammonia rinse solution

Preparation of 2) – 5) above is the same as described in a) Note 1) – 4).

**Procedures:**

1) Sample measurement is the same as that described for As Procedures 1).
2) For the standard solutions to be used for generating the calibration curve, transfer 0 – 4.0m*l* of Sb standard solution (1µg of Sb/m*l*) in increasing concentrations (containing 0

– 4µg of Sb) to several beakers. After adding 60m*l* of nitric acid (1+1) to each beaker, add water to bring total volume to about 200m*l*. Add both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to these beakers. While mixing, add 160m*l* of aqueous ammonia. Heat this solution and boil gently for 5 minutes. Filter out the precipitate using Type 5B filter paper, and rinse several times using warm ammonium rinse solution. Discard the rinse liquid and filtrate.

Using warm water, rinse the precipitate on the filter paper back into the original beaker. Place the beaker under the funnel, and drip 10m*l* of the nitric acid mixture onto the filter paper to dissolve any remaining precipitate. Rinse the filter paper thoroughly using warm nitric acid (1+50). Heat both the filtrate and rinse solution until the precipitate is completely dissolved, then transfer the solution to a 200m*l* beaker using a small amount of water. Heat again to concentrate, and after cooling to ambient temperature, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water. Use this solution for measurement.

**Measurement:**

| | | |
|---|---|---|
| Measurement wavelength | : | 217.6nm |
| Calibration curve range | : | 2 – 40 ng/m*l* |
| Tube | : | High density graphite tube |
| Sample injection volume | : | 20µ*l* |
| Heating conditions | : | |

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2200 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

### 15.3.3 Flame Atomic Absorption Method

#### a) Target element and quantitation range

| Element | Percent contained (%) |
|---|---|
| Bi | 0.0001 – 0.01 |
| Fe | 0.0001 – 0.01 |
| Pb | 0.0001 – 0.01 |
| Sb | 0.0001 – 0.01 |

#### b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- **Bi**

**Reagents:**

1) Bi standard solution (50µg of Bi/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution
3) Lanthanum nitrate solution

Preparation of 2), 3) above is the same as described in a) Note 1), 2).

**Procedures:**

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, perform the same pretreatment procedure on the reagent containing no sample. Measure this solution, and use the value obtained to correct the value obtained in sample measurement.
2) For the standard solutions to be used for generating the calibration curve, transfer both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to several 25m*l* volumetric flasks, and add increasing volumes of the Bi standard solution (50µg of Bi/m*l*) from 0 – 5.0m*l* (Bi content from 0 – 250µg). After adding 2m*l* of nitric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

Measurement wavelength : 223.1nm
Calibration curve range : 1 – 10µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 8)

- **Fe**

**Reagents:**

Fe standard solution (10µg of Fe/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.

Procedure:

1) The sample solution pretreated according to step c) is measured just as it is. For blank measurement, perform the same pretreatment procedure on the reagent containing no sample, measure this solution, and use the value obtained to correct the value obtained in sample measurement.
2) For the standard solutions to be used for generating the calibration curve, transfer increasing volumes of the Fe standard solution (10µg of Fe/m*l*) from 0 – 5.0m*l* (Fe content from 0 – 50µg) to several 25m*l* volumetric flasks. After adding 50m*l* of hydrochloric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

Measurement wavelength : 248.3nm
Calibration curve range : 0.2 – 2µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- **Pb**

**Reagents:**

1) Pb standard solution (50µg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution
3) Lanthanum nitrate solution

   Preparation of 2), 3) above is the same as described in a) Note 1), 2).

**Procedures:**

1) Sample measurement is conducted using the same procedure as that described for Bi, Procedure, 1).
2) For the standard solutions to be used in generating the calibration curve, transfer both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to several 25m*l* volumetric flasks. Add increasing volumes of the Pb standard solution (50µg of Pb/m*l*) from 0 – 5.0m*l* (Pb content from 0 – 250µg), and after adding 2m*l* of nitric acid (1+1) to each of the flasks, bring up to volume with water.

**Measurement:**

Measurement wavelength : 283.3nm
Calibration curve range : 1 – 10µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

- **Sb**

**Reagents:**

1) Sb standard solution (50µg of Sb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Iron (III) solution
3) Lanthanum nitrate solution
4) Nitric acid mixture
5) Ammonia rinse solution

Preparation of 2) – 5) above is the same as described in a) Note 1) – 4).

**Procedures:**

1) Sample measurement is the same as that described for Bi Procedure 1).
2) For the standard solutions to be used in generating the calibration curve, transfer 0 – 5.0m*l* of Sb standard solution (50µg of Sb/m*l*) in increasing concentrations (containing 0 – 250µg of Sb) to several 500m*l* beakers. After adding 60m*l* of nitric acid (1+1) to each beaker, add water to bring total volume to about 200m*l*. Add both 4m*l* of the iron (III) solution and 4m*l* of the lanthanum nitrate solution to these beakers. While mixing add 160m*l* of aqueous ammonia. Heat this solution and boil gently for 5 minutes. Filter out the precipitate using Type 5B filter paper, and rinse several times using warm ammonium rinse solution. Discard the rinse liquid and filtrate.

   Using warm water, rinse the precipitate on the filter paper back into the original beaker. Place the beaker under the funnel, and drip 10m*l* of the nitric acid mixture onto the filter paper to dissolve any remaining precipitate. Rinse the filter paper thoroughly using warm nitric acid (1+50). Heat both the filtrate and rinse solution until the precipitate is completely dissolved, and then transfer the solution to a 200m*l* beaker using a small amount of water. Heat again to concentrate, and after cooling to ambient temperature, transfer to a 25m*l* volumetric flask using water, and bring up to volume with water. Use this solution for measurement.

**Measurement:**

Measurement wavelength : 217.6nm

Calibration curve range : 1 – 10µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 32)

## 15.4 Aluminum and Aluminum Alloy Analysis Method

Reference materials:

Japan Industrial Standard, Aluminum and Aluminum Alloy Atomic Absorption Analysis Method JIS H 1306

### 15.4.1 Sample Pretreatment

**a) Weighing out sample**

The sample weight is based on the amount of the target element contained in the sample. The following table gives sample weights based on the percentage of target element in the sample.

| Element | Percent contained (%) | Weight (g) |
|---|---|---|
| Bi | 0.1 – 1.0 | 1.00 |
| Cr | 0.01 – 0.5 | 1.00 |
| Cu | 0.005 – 1.5 | 1.00 |
|  | 1.5 – 5.0 | 0.20 |
| Fe | 0.005 – 1.5 | 1.00 |
| Mn | 0.005 – 1.5 | 1.00 |
| Mg | 0.005 – 1.5 | 1.00 |
|  | 1.5 – 5.0 | 0.20 |
| Ni | 0.005 – 1.5 | 1.00 |
|  | 1.5 – 3.0 | 0.20 |
| Pb | 0.1 – 1.0 | 1.00 |
| Zn | 0.005 – 1.5 | 1.00 |
|  | 1.5 – 6.0 | 0.20 |

**b) Preparing sample solution**

Weigh out the sample and transfer it to a 300m*l* beaker. Cover with a watch glass, add 30m*l* of hydrochloric acid (1+1) and heat gently to decompose. To this solution add 1m*l* of hydrogen peroxide, and heat to completely decompose the sample. Cool to ambient temperature, and then rinse the bottom of the watch glass and inner wall of the beaker with water. Then remove the watch glass. Transfer the solution to a 100m*l* volumetric flask, and add water to bring up volume.

Note:

1) For Cr, transfer the solution to a 200m*l* volumetric flask, add 1.5m*l* of ammonium hydrochloride solution (270g/*l*), and bring up to volume with water.
2) When the contained percentages of Cu, Zn, Mg and Ni are greater than 1.5%, transfer the solution containing the decomposed sample to a 200m*l* volumetric flask.
3) For samples that are difficult to decompose, add 2m*l* of tin solution or 2m*l* of nickel solution.
4) Tin solution: Weigh out 0.1g of tin (>99.9%), transfer to a 200m*l* beaker, add 30m*l* of hydrochloric acid (1+1). While placing in contact with platinum, heat at 50 – 80°C to

decompose. Then cool to ambient temperature, and add hydrochloric acid to bring up to 100m*l*.

5) Nickel solution: Weigh out 0.1g of nickel (>99.9%), transfer to a 200m*l* beaker, add 10m*l* of nitric acid (1+1), and heat gently to decompose. Cool to ambient temperature and add water to bring volume to 100m*l*.

### 15.4.2 Flame Atomic Absorption Method

#### a) Target element and quantitation range

| Element | Percent contained (%) |
|---|---|
| Bi | 0.1 – 1.0 |
| Cr | 0.01 – 0.5 |
| Cu | 0.005 – 5.0 |
| Fe | 0.005 – 1.5 |
| Mn | 0.005 – 1.5 |
| Mg | 0.005 – 5.0 |
| Ni | 0.005 – 3.0 |
| Pb | 0.1 – 1.0 |
| Zn | 0.005 – 6.0 |

#### b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- **Bi**

**Reagents:**

Bi standard solution (1000µg of Bi/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.

**Procedure:**

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Bi standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, measure out 1.0gram of aluminum (as pure as possible, containing no Bi or containing a known quantity of Bi) for each solution, and transfer these to several 300m*l* beakers. To these

beakers, transfer increasing volumes of Bi standard solution (1000µg of Bi/m*l*) from 0 – 10.0m*l* (containing 0 – 10µg of Bi). The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

**Measurement:**

Measurement wavelength : 223.1nm
Calibration curve range : 1 – 100µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 8)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- **Cr**

**Reagents:**

1) Cr standard solution (1000µg of Cr/m*l*)
2) Cr standard solution (100µg of Cr/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

**Procedure:**

1) The pretreated sample solution can be measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cr standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, measure out 1.0gram of aluminum (as pure as possible, containing no Cr or containing a known quantity of Cr) for each solution, and transfer these to several 300m*l* beakers. Depending on the amount of Cr contained in the sample, Cr standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Cr in Sample (%) | Cr standard used | Amt of Cr added (m*l*) |
|---|---|---|
| 0.01 – 0.1 | 2) 100µg of Cr/m*l* | 0 – 10.0 |
| >0.1 | 1) 1000µg of Cr/m*l* | 0 – 5.0 |

**Measurement:**

Measurement wavelength : 357.9nm

Calibration curve range : 0.3 – 25µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 13)

**Note:** If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- **Cu**

**Reagents**:

1) Cu standard solution (1000µg of Cu/m*l*)
2) Cu standard solution (100µg of Cu/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

**Procedure:**

1) When the pretreated sample solution contains less than 0.1 % of Cu, it can be measured just as it is. However, if the pretreated sample solution contains more than 0.1%, use an aliquot indicated in the following table for measurement.

| Percent Cu in Sample (%) | Aliquot (m*l*) | Volumetric flask |
|---|---|---|
| 0.1 – 0.5 | 50 | 100 |
| 0.5 – 1.5 | 20 | 100 |
| 1.5 – 5.0 | 20 | 200 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out aluminum (as pure as possible, containing no Cu or containing a known quantity of Cu) to the same weight within 10mg of the sample pretreated according to step a) of the pretreatment description for sample. Transfer this quantity to several 300m*l* beakers. Depending on the amount of Cu contained in the sample, Cu standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b)

Preparing sample solutions.

| Percent Cu in Sample (%) | Cu standard used | Amt of Cu added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100µg of Cu/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000µg of Cu/m*l* | 0 – 5.0 |
| 0.5 – 1.5 | 1) 1000µg of Cu/m*l* | 0 – 15.0 |
| 1.5 – 5.0 | 1) 1000µg of Cu/m*l* | 0 – 10.0 |

**Measurement:**

Measurement wavelength : 324.8nm

Calibration curve range : 0.2 – 30µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- **Fe**

**Reagents:**

1) Fe standard solution (1000µg of Fe/m*l*)
2) Fe standard solution (100µg of Fe/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

**Procedure:**

1) When the pretreated sample solution contains less than 0.1% of Fe, it can be measured just as it is. However, if the pretreated sample solution contains more than 0.1%, use an aliquot indicated in the following table for measurement.

| Percent Cu in Sample (%) | Aliquot (m*l*) | Volumetric flask |
|---|---|---|
| 0.1 – 0.5 | 50 | 100 |
| 0.5 – 1.5 | 20 | 100 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out 1.0gram of aluminum (as pure as possible, containing no Fe or containing a known quantity of Fe) for each solution, and transfer these to several 300m*l* beakers. Depending on the amount of Fe contained in the sample, Fe standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Fe in Sample (%) | Fe standard used | Amt of Fe added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100μg of Fe/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000μg of Fe/m*l* | 0 – 5.0 |
| 0.5 – 1.5 | 1) 1000μg of Fe/m*l* | 0 – 15.0 |

**Measurement:**

Measurement wavelength : 248.3nm
Calibration curve range : 0.3 – 30μg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Mn

Reagents:

1) Mn standard solution (1000μg of Mn/m*l*)
2) Mn standard solution (100μg of Mn/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

**Procedure:**

1) When the pretreated sample solution contains less than 0.1% of Mn, it can be measured just as it is. However, if the pretreated sample solution contains more than 0.1%, use an aliquot indicated in the following table for measurement.

| Percent Mn in Sample (%) | Aliquot (m*l*) | Volumetric flask |
|---|---|---|
| 0.1 – 0.5 | 50 | 100 |
| 0.5 – 1.5 | 20 | 100 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mn standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out 1.0gram of aluminum (as pure as possible, containing no Mn or containing a known quantity of Mn) for each solution, and transfer these to several 300m*l* beakers. Depending on the amount of Mn contained in the sample, Mn standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Mn in Sample (%) | Mn standard used | Amt of Mn added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100μg of Mn/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000μg of Mn/m*l* | 0 – 5.0 |
| 0.5 – 1.5 | 1) 1000μg of Mn/m*l* | 0 – 15.0 |

Measurement:

Measurement wavelength : 279.5nm

Calibration curve range : 0.2 – 30μg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 22)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Mg

Reagents:

1) Mg standard solution (1000μg of Mg/m*l*)

2) Mg standard solution (100μg of Mg/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

3) Strontium solution: Dissolve 30.8g of strontium chloride 6-hydrate in water, and add water to bring solution up to 100m*l*.

Procedure:

1) Prepare an aliquot from the pretreated sample solution according to the following table, and use that aliquot for measurement.

| Percent Mg in Sample (%) | Aliquot (m*l*) | Amt of Sr Added (m*l*) | Volumetric flask |
|---|---|---|---|
| 0.005 – 0.1 | 20.0 | 2.0 | 100 |
| 0.1 – 0.5 | 10.0 | 2.0 | 100 |
| 0.5 – 1.5 | 5.0 | 2.0 | 100 |
| 1.5 – 5.0 | 5.0 | 2.0 | 100 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mg standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out aluminum (as pure as possible, containing no Mg or containing a known quantity of Mg) to the same weight within 10mg of the sample pretreated according to step a) of the pretreatment description for sample. Transfer this quantity to several 300m*l* beakers. Depending on the amount of Mg contained in the sample, Mg standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Mg in Sample (%) | Mg standard used | Amt of Mg added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100μg of Mg/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000μg of Mg /m*l* | 0 – 5.0 |
| 0.5 – 1.5 | 1) 1000μg of Mg /m*l* | 0 – 15.0 |
| 1.5 – 5.0 | 1) 1000μg of Mg /m*l* | 0 – 10.0 |

Measurement:

Measurement wavelength : 285.2nm

Calibration curve range : 0.2 – 7.5µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 21)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Ni

Reagents:

1) Ni standard solution (1000µg of Ni /m*l*)
2) Ni standard solution (100µg of Ni /m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

Procedure:

1) When the pretreated sample solution contains less than 0.1% of Ni, it can be measured just as it is. However, if the pretreated sample solution contains more than 0.1%, use an aliquot indicated in the following table for measurement.

| Percent Ni in Sample (%) | Aliquot (m*l*) | Volumetric flask |
|---|---|---|
| 0.1 – 0.5 | 50 | 100 |
| 0.5 – 1.5 | 20 | 100 |
| 1.5 – 5.0 | 20 | 100 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Ni standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out aluminum (as pure as possible, containing no Ni or containing a known quantity of Ni) to the same weight within 10mg of the sample pretreated according to step a) of the pretreatment description for sample. Transfer this quantity to several 300m*l* beakers. Depending on the amount of Ni contained in the sample, Ni standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Ni in Sample (%) | Ni standard used | Amt of Ni added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100µg of Ni/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000µg of Ni/m*l* | 0 – 5.0 |
| 0.5 – 1.5 | 1) 1000µg of Ni/m*l* | 0 – 15.0 |
| 1.5 – 3.0 | 1) 1000µg of Ni/m*l* | 0 – 10.0 |

Measurement:

Measurement wavelength : 232.0nm

Calibration curve range : 0.5 – 30µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 25)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Pb

Reagents:

Pb standard solution (1000µg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.

Procedure:

1) Sample measurement is conducted as described for Bi, Procedure, Step 1).
2) For the standard solutions to be used in generating the calibration curve, measure out 1.0gram of aluminum (as pure as possible, containing no Pb or containing a known quantity of Pb) for each solution, and transfer these to several 300m*l* beakers. To these beakers, transfer increasing volumes of Pb standard solution (1000µg of Pb/m*l*) from 0 – 10.0m*l* (containing 0 – 10mg of Pb). The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

Measurement:

Measurement wavelength : 283.3nm

Calibration curve range : 1 – 100µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Zn

Reagents:

1) Zn standard solution (1000µg of Zn/m*l*)
2) Zn standard solution (100µg of Zn/m*l*)

For Preparation of 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards.

Procedure:

1) For measurement, use an aliquot of the pretreated sample as indicated in the following table.

| Percent Zn in Sample (%) | Aliquot (m*l*) | Volumetric flask |
|---|---|---|
| 0.005 – 0.1 | 50.0 | 100 |
| 0.1 – 0.5 | 20.0 | 100 |
| 0.5 – 1.5 | 5.0 | 100 |
| 1.5 – 6.0 | 10.0 | 100 |

For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Zn standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, measure out aluminum (as pure as possible, containing no Zn or containing a known quantity of Zn) to the same weight within 10mg of the sample pretreated according to step a) of the pretreatment description for sample. Transfer this quantity to several 300m*l* beakers. Depending on the amount of Zn contained in the sample, Zn standard solution is added to the beakers in increasing concentrations as indicated in the table below. The remainder of the procedure is the same as that described for Sample Pretreatment b) Preparing sample solutions.

| Percent Zn in Sample (%) | Zn standard used | Amt of Zn added (m*l*) |
|---|---|---|
| 0.005 – 0.1 | 2) 100µg of Zn/m*l* | 0 – 10.0 |
| 0.1 – 0.5 | 1) 1000µg of Zn/m*l* | 0 – 5.0 |

| | | |
|---|---|---|
| 0.5 – 1.5 | 1) 1000μg of Ni/m*l* | 0 – 15.0 |
| 1.5 – 6.0 | 1) 1000μg of Ni/m*l* | 0 – 12.0 |

Measurement:

Measurement wavelength : 213.9nm

Calibration curve range : 0.1 – 10μg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 44)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

## 15.5 Die cast Zinc Alloy Analysis Method

Reference materials:

Japan Industrial Standard, Die cast Zinc Alloy Analysis Method JIS H 1551

### 15.5.1 Sample Pretreatment

a) Al, Cd, Cu, Fe Mg, Pb

Weigh out 5.0g of sample to the nearest 1mg, and transfer to a 300m*l* beaker. Cover with a watch glass, and add 30m*l* of the acid mixture (45 parts hydrochloric acid, 1 part nitric acid) to decompose. After the intense reaction subsides, keep heating gently until decomposition is complete and the total volume has decreased to about 25m*l*. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. After adding about 20m*l* of water and 20m*l* of hydrochloric acid (1+1), transfer the solution to a 100m*l* volumetric flask and bring up to volume with water.

b) Sn

Weigh out 1.0g of sample to the nearest 10mg, and transfer to a 300m*l* beaker. Cover with a watch glass, and add 20m*l* of nitric (1+2), and after the intense reaction subsides, keep heating gently until decomposition is complete. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. Transfer the solution to a 100m*l* volumetric flask and bring up to volume with water.

### 15.5.2 Electrical Heating Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Sn | 0.0001 – 0.004 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current and slit width, refer to Cookbook Section 4, Item 7.5 Element Specific Measurement Conditions.

- Sn

Reagents:

1) Sn standard solution (2µg of Sn/m*l*)
2) Cu standard solution (1µg of Cu/m*l*)
   For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
3) Zn: >99.99%, containing <0.00005% Sn
4) Aluminum solution (2µg Al/m*l*): Weigh out 0.500g of aluminum (>99.9%, containing <0.0025% Sn), transfer to a 300m*l* beaker, add 20m*l* of nitric acid (1+2) and 2m*l* of nickel solution (1g of nickel nitrate 6-hydrate dissolved in 250m*l* of water) to decompose. After cooling to ambient temperature, transfer solution to a 250m*l* volumetric flask using water, and bring up to volume with water.

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Sn standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, weigh out 1.0gram of Zn into each of several 300m*l* beakers, and add 20m*l* of nitric acid (1+2) to decompose. After cooling to ambient temperature, transfer each of these solutions to a 100m*l* volumetric flask using water. Then add 20m*l* of aluminum solution (2mg of Al/m*l*) and 10m*l* of Cu standard solution (1mg of Cu/m*l*). To these, add increasing volumes of Sn standard solution (2µg of Sn/m*l*) from 0 – 20.0m*l* (containing 0 – 40µg of Sn). Finally, bring up to volume with water.

Note: If the sample contains less than 0.25% Cu, do not add the Cu standard solution.

Measurement:

Measurement wavelength : 286.3nm
Calibration curve range : 10 – 400 ng/m*l*
Tube : Pyrolized graphite tube
Sample injection volume : 10µ*l*
Heating conditions :

| TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|

|  |  |  |  |  |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 500 | 10 | R | 1.0 |
| 4 | 500 | 10 | R | 1.0 |
| 5 | 500 | 3 | S | 0.0 |
| 6 | 2400 | 3 | S | 0.0 |
| 7 | 2800 | 2 | S | 1.0 |

### 15.5.3 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Al | 3.0 – 5.0 |
| Cd | 0.0001 – 0.010 |
| Cu | 0.005 – 2.0 |
| Fe | 0.0002 – 0.20 |
| Mg | 0.002 – 0.10 |
| Pb | 0.001 – 0.010 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Al

Reagents:

1) Al standard solution (1g of Al/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn standard solution (25mg of Zn/m*l*): Weigh out 25.0g of zinc (>99.995%), transfer to a 500m*l* beaker, add 100m*l* of hydrochloric acid (1+1) to decompose, and heat to concentrate to a syrupy consistency. After cooling to room temperature, add about 200m*l* of water to dissolve the salts. Transfer the solution to a 1000m*l* volumetric flask using water, and bring up to volume with water.

Procedure:

1) Accurately transfer 5m*l* of sample solution pretreated according to step a) to a 250m*l* volumetric flask, add 50m*l* of hydrochloric acid (1+1), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Al standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, transfer 10m*l* of zinc solution (25mg of Zn/m*l*) to each of several 250m*l* volumetric flasks, and add 50m*l* of hydrochloric acid (1+1) to each flask. Add Al standard solution (1mg of Al/m*l*) in increasing volumes from 0 – 15.0m*l* (containing 0 – 150m*l* of Al), and bring the solutions up to volume with water.

Measurement:

Measurement wavelength : 309.3nm
Calibration curve range : 10 – 60μg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 2)

- Cd

Reagents:

1) Cd standard solution (20mg of Cd/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn standard solution (192μg of Zn/m*l*): Weigh out 96g of zinc (>99.995%), transfer to a 1000m*l* beaker, add 400m*l* of hydrochloric acid (1+1) to decompose. Heat to concentrate to a syrupy consistency. After cooling to room temperature, add about 400m*l* of water to dissolve the salts, and transfer the solution to a 500m*l* volumetric. Add about 20g of powdered zinc (JIS K 8013) and set aside for about 30 minutes, occasionally shaking the flask, and then bring up to volume with water. Filter this solution through type 5B dry filter paper into a container, which can be sealed.
3) Aluminum solution (20mg of Al/m*l*): weigh out 2.0g aluminum (>99.9%, containing <0.0002% of cadmium), transfer to a 300m*l* beaker, add 40m*l* of hydrochloric acid (1+1) and 2m*l* of nickel solution (1g of nickel chloride) dissolved in 250m*l* of water), add 1 – 2m*l* of nitric acid, and heat to dissolve the remaining undissolved aluminum. Then continue heating to drive off the hydrogen peroxide. After cooling to ambient temperature, transfer the solution to 100m*l* volumetric flask using water, and bring up to volume with water.

Procedure:

1) The sample solution pretreated according to step a) is measured just as it is. For blank

measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cd standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, transfer 25m*l* of Zn standard solution (192mg of Zn/m*l*): and 10m*l* of aluminum solution (20mg of Al/m*l*) to each of several 100m*l* volumetric flasks, and add 20m*l* of hydrochloric acid (1+1) to each flask. Add Cd standard solution (20µg of Cd/m*l*) in increasing volumes from 0 – 25.0m*l* (containing 0 – 500µg of Cd), and bring the solutions up to volume with water.

Measurement:

Measurement wavelength : 228.8nm
Calibration curve range : 0.05 – 5µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4,11)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Cu

Reagents:

1) Cu standard solution (250µg of Cu/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn solution (192mg of Zn/m*l*): Same procedure as that for Cd Reagent, 2)
3) Zn solution (25mg of Zn/m*l*): Same procedure as that for Al Reagent, 2)
4) Aluminum solution (20mg of Al/m*l*): Same procedure as that for Cd Reagent, 3)

Procedure:

1) When the sample solution pretreated according to step a) contains from 0.005 – 0.05% Cu, it is measured just as it is. However, if the amount of Cu in the sample is 0.05 – 2.0%, accurately transfer 5m*l* of the sample solution to a 250m*l* volumetric flask, add 50m*l* of hydrochloric acid (1+1), and bring up to volume with water. Use this solution for measurement.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, when the sample

contains from 0.005 – 0.05% Cu, transfer 25m*l* of Zn standard solution (192mg of Zn/m*l*): and 10m*l* of aluminum solution (20mg of Al/m*l*) to each of several 100m*l* volumetric flasks, and add 20m*l* of hydrochloric acid (1+1) to each flask. Add Cu standard solution (250µg of Cu/m*l*) in increasing volumes from 0 – 10.0m*l* (containing 0 – 2.5µg of Cd), and bring the solutions up to volume with water.

When the sample contains from 0.05 – 2.0% Cu, transfer 10m*l* of zinc solution (25mg of Zn/m*l*) to each of several 250m*l* volumetric flasks, and add 50m*l* of hydrochloric acid (1+1). Add Cu standard solution (250µg of Cu/m*l*) in incremental volumes from 0 – 20.0m*l* (containing 0 – 5µg of Cu) to the flasks, and bring up to volume with water.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.5 – 25µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

Reagents:

1) Fe standard solution (20µg of Fe/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn solution (192mg of Zn/m*l*):: Same procedure as that for Cd Reagent, 2)
3) Aluminum solution (20mg of Al/m*l*): Same procedure as that for Cd Reagent, 3)

Procedure:

1) When the sample solution pretreated according to step a) contains from 0.0002 – 0.016 % Fe, it is measured just as it is. However, if the amount of Fe in the sample is 0.016 – 0.20%, accurately transfer 5m*l* of the sample solution to a 100m*l* volumetric flask. Add 20m*l* of hydrochloric acid (1+1), and bring up to volume with water. Use this solution for measurement.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, when the sample contains from 0.0002 – 0.016% Fe, transfer 25m*l* of Zn standard solution (192mg of Zn/m*l*), and 10m*l* of aluminum solution (20mg of Al/m*l*) to each of several 100m*l* volumetric flasks. Add 20m*l* of hydrochloric acid (1+1) to each flask. Add Fe

standard solution (20µg of Fe/m*l*) in increasing volumes from 0 – 40.0m*l* (containing 0 – 800µg of Fe), and bring the solutions up to volume with water.

When the sample contains from 0.016 – 0.20% Fe, transfer 1.3m*l* of zinc solution (192mg of Zn/m*l*) and 0.5m*l* of aluminum solution (20mg of Al/m*l*) to each of several 100m*l* volumetric flasks, and add 20m*l* of hydrochloric acid (1+1). Add Fe standard solution (20µg of Fe/m*l*) in incremental volumes from 0 – 30.0m*l* (containing 0 – 600µg of Fe) to the flasks, and bring up to volume with water.

Measurement:

| | | |
|---|---|---|
| Measurement wavelength | : | 248.3nm |
| Calibration curve range | : | 0.1 – 8µg /m*l* |
| Measurement conditions | : | Refer to Cookbook Section 3, Item 6.4, 16) |

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Mg

Reagents:

1) Mg standard solution (10µg of Mg/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn solution (25mg of Zn/m*l*): Same procedure as that for Al Reagent, 2)
3) Lanthanum solution (25mg of La/m*l*): Weigh out 29.5g of lanthanum oxide, transfer it to a 500m*l* beaker, gradually add 30m*l* of hydrochloric acid. After adding 200m*l* of water, heat until completely decomposed. Cool to ambient temperature, then transfer the solution to a 1000m*l* volumetric flask and bring up to volume with water.

Procedure:

1) Accurately transfer 250m*l* of sample solution pretreated according to step a) to a 250m*l* volumetric flask. Add 50m*l* of hydrochloric acid (1+1) and 25m*l* of lanthanum solution (25mg of La/m*l*), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mg standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, transfer 10m*l* of Zn solution (25mg of Zn/m*l*): to each of several 250m*l* volumetric flasks, and add 50m*l* of hydrochloric acid (1+1) to each of the flasks. Add increasing volumes of Mg standard solution (10µg of Mg/m*l*) from 0 – 25.0m*l* (containing 0 – 250µg of Mg) to each of the flasks, add 25m*l* lanthanum solution (25mg of La/m*l*), and then bring up to

volume with water.

Measurement:

Measurement wavelength : 285.2nm

Calibration curve range : 0.02 – 1µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 21)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Pb

Reagents:

1) Pb standard solution (20µg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn solution (192mg of Zn/m*l*): Same procedure as that for Cd Reagent, 2)
3) Aluminum solution (20mg of Al/m*l*): Same procedure as that for Cd Reagent, 3)

Procedure:

1) The sample solution pretreated according to step a) is measured just as it is.
   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Pb standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, transfer 25m*l* of Zn standard solution (192mg of Zn/m*l*), and 10m*l* of aluminum solution (20mg of Al/m*l*) to each of several 100m*l* volumetric flasks. Add 20m*l* of hydrochloric acid (1+1) to each flask. Add Pb standard solution (20µg of Pb/m*l*) in increasing volumes from 0 – 25.0m*l* (containing 0 – 500µg of Pb), and bring the solutions up to volume with water.

Measurement:

Measurement wavelength : 217.0nm

Calibration curve range : 0.5 – 5µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 26)

### 15.6 Zinc Alloy Analysis Method

Reference materials: Japan Industrial Standard:

| | |
|---|---|
| Zinc Alloy Lead Quantitation Method | JIS H 1108 |
| Zinc Alloy Iron Quantitation Method | JIS H 1109 |
| Zinc Alloy Cadmium Quantitation Method | JIS H 1110 |

#### 15.6.1 Sample Pretreatment

a) Cd, Fe, Pb

Weigh out 5.0g of sample and transfer to a 300m*l* beaker. Cover with a watch glass, and add 30m*l* of acid mixture (45 parts hydrochloric acid, 1 part nitric acid). After the intense reaction subsides, keep heating gently until decomposition is complete and the total volume has decreased to about 25m*l*. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. After adding about 20m*l* of water and 20m*l* of hydrochloric acid (1+1), transfer the solution to a 100m*l* volumetric flask and bring up to volume with water.

b) Pb (Iron hydroxide precipitation separation)

Weigh out 100g of sample, transfer to a 500m*l* beaker, and add 5m*l* of ferric ammonium sulfate (III). Cover with a watch glass, and add 60m*l* of acid mixture (45 parts hydrochloric acid, 1 part nitric acid). After the intense reaction subsides, keep heating gently until decomposition is complete and the total volume has decreased to about 25m*l*. After cooling to ambient temperature, rinse the bottom of the watch glass with water. Remove the watch glass, and add water to bring the volume to about 200m*l*.

While mixing this solution, add aqueous ammonia to dissolve the zinc hydroxide precipitate. After it dissolves, add 50m*l* more. Next add 15g of ammonium carbonate and heat. After boiling gently for about 5 minutes, set aside in a warm location (60 – 80°C) for 1 – 2 hours. Separate the precipitate using Type 5A filter paper, and rinse several times with warm ammonia rinse solution.

Transfer the precipitate on the filter paper to the original beaker by rinsing with warm water. Place the beaker under the filter, and drip 10m*l* of hydrochloric acid (1+1) onto the filter paper to dissolve the remaining precipitate on the filter paper and in the beaker. Rinse the filter paper thoroughly with warm hydrochloric acid (1+50).

Heat the combined filtrate and rinse solution to concentrate it to a volume of 10 – 20m*l*. After cooling, transfer to a 50m*l* volumetric flask using water, and bring up to volume with water.

Note: Ferric ammonium sulfate (III) solution: Dissolve 10g of ferric ammonium sulfate in 100m*l* of nitric acid (1+100). 1m*l* of this solution contains 12mg of Fe.

Ammonium rinse solution: Dissolve 15g of ammonium carbonate in 500m*l* of aqueous ammonia (2+25).

### 15.6.2 Flame Atomic Absorption Method

a) Target Element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Cd | 0.0001 – 1.0 |
| Fe | 0.0002 – 0.3 |
| Pb | 0.001 – 2.0 |
| Pb | 0.0001 – 0.02 (Iron hydroxide precipitation |

separation)

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Cd

Reagents:

1) Cd standard solution (20µg of Cd/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Zn solution: Decompose 100g of zinc (99.995wt%) in 400m*l* of hydrochloric acid, and heat until concentrated to a syrupy consistency. After cooling to ambient temperature, add 400m*l* to dissolve, and transfer to a 500m*l* volumetric flask. Add 20g of powdered zinc (for arsenic reagent analysis), and set aside for about 30 minutes, shaking occasionally to mix. After bringing up to volume with water, pass the solution through Type 5A dry filter paper. (200mg of Zn/m*l*)

Procedure:

1) The sample solution pretreated according to step a) can be measured directly, or use an aliquot (to which hydrochloric acid (1+1) is added so that the ratio of hydrochloric acid to sample solution is 10m*l* /100m*l*) for measurement.

   For blank measurement, perform the same pretreatment on the reagent as that for the sample, diluting only the standard solution. The value obtained from measuring this solution can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, transfer 25m*l* of Zn solution (200mg of Zn/m*l*) to each of several 100m*l* volumetric flasks. Add 20m*l* of hydrochloric acid (1+1) to each flask. Add Cd standard solution (20µg of Cd/m*l*) in increasing volumes from 0 – 30.0m*l* (containing 0 – 600µg of Cd), and bring the solutions up to volume with water. If an aliquot of the sample solution was used, the volume of zinc solution added should be adjusted so that it contains about the same amount of zinc in the sample aliquot.

Measurement:

Measurement wavelength : 228.8nm
Calibration curve range : 0.1 – 6µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 11)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

  Reagents:

  1) Fe standard solution (20μg of Fe/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
  2) Zn solution: Same as for Cd, Reagent, 2)

  Procedure:

  1) Same as for Cd, Procedure, 1)
  2) For the standard solutions to be used in generating the calibration curve, transfer 25m*l* of Zn solution (200mg of Zn/m*l*) to each of several 100m*l* volumetric flasks. Add 20m*l* of hydrochloric acid (1+1) to each flask. Add Fe standard solution (20μg of Fe/m*l*) in increasing volumes from 0 – 40.0m*l* (containing 0 – 800μg of Fe), and bring the solutions up to volume with water. If an aliquot of the sample solution was used, the volume of zinc solution added should be adjusted so that it contains about the same amount of zinc in the sample aliquot.

  Measurement:

  Measurement wavelength : 248.3nm
  Calibration curve range : 0.5 – 8μg /m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 17)

  Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Pb

  Reagents:

  1) Pb standard solution (20μg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
  2) Zn solution: Same as for Cd, Reagent, 2)

  Procedure:

  1) Same as for Cd, Procedure, 1)
  2) For the standard solutions to be used in generating the calibration curve, transfer 25m*l* of Zn solution (200mg of Zn/m*l*) to each of several 100m*l* volumetric flasks. Add 20m*l* of hydrochloric acid (1+1) to each flask. Add Pb standard solution (20μg of Pb/m*l*) in increasing volumes from 0 – 50.0m*l* (containing 0 – 1000μg of Pb), and bring the solutions up to volume with water. If an aliquot of the sample solution was used, the

volume of zinc solution added should be adjusted so that it contains about the same amount of zinc in the sample aliquot.

Measurement:

Measurement wavelength : 283.3nm
Calibration curve range : 1 – 10μg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

- Pb (Iron hydroxide precipitation separation)

Reagents:

1) Pb Standard solution (20μg of Pb/m*l*): Same as Pb, Reagent, 1)
2) Ferric ammonium sulfate (III) solution: Same as described in Note for Sample Pretreatment, Pb (Iron hydroxide precipitation separation)

Procedure:

1) The sample solution pretreated according to step b) may be measured just as it is. For blank measurement, perform the same pretreatment on the reagent only as that performed on the sample. The value obtained from measuring this solution can be used to correct the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, transfer 5m*l* of the ferric ammonium sulfate (III) solution to each of several 50m*l* volumetric flasks, and add 10m*l* of hydrochloric acid (1+1) to each flask. Add Pb standard solution (20μg of Pb/m*l*) in increasing volumes from 0 – 50.0m*l* (containing 0 – 500μg of Pb), and bring the solutions up to volume with water. Use these solutions for generating the calibration curve.

Measurement:

Measurement wavelength : 217.0nm
Calibration curve range : 0.5 – 5μg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 26)

## 15.7 Nickel and Nickel Alloy Cast Metal Analysis Method

Reference materials: Japan Industrial Standard

| | |
|---|---|
| Nickel / Nickel Alloy Cast Metal Lead Quantitation Method | JIS H 1272 |
| Nickel / Nickel Alloy Cast Metal Iron Quantitation Method | JIS H 1273 |
| Nickel / Nickel Alloy Cast Metal Manganese Quantitation Method | JIS H 1274 |
| Nickel Alloy Cast Metal Chrome Quantitation Method | JIS H 1279 |

### 15.7.1 Sample Pretreatment

a) Cr

Weigh out 0.20g of sample and transfer to a 200m*l* beaker. Cover with a watch glass, add 10m*l* of hydrochloric acid and 3m*l* of nitric acid. Heat gently until decomposition is complete, and then continue heating until the nitrogen oxide is driven off. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. Then transfer the solution to a 100m*l* volumetric flask, and after adding 10m*l* of potassium disulfide (100 g/*l*), bring up to volume with water.

b) Cu, Fe, Mn

Weigh out 0.20g of sample and transfer to a 200m*l* beaker. Cover with a watch glass, add 20m*l* of nitric acid (1+1). Heat gently until decomposition is complete, and then continue heating until the nitrogen oxide is driven off. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. Then transfer the solution to a 100m*l* volumetric flask and bring up to volume with water.

### 15.7.2 Flame Atomic Absorption Method

a) Target Element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Cr | 0.05 – 2.0 |
| Cu | 0.05 – 2.0 |
| Fe | 0.05 – 2.0 |
| Mn | 0.05 – 2.0 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Cr

Reagents:

1) Cr standard solution (100µg of Cr/m*l*)
2) Cr standard solution (500µg of Cr/m*l*)

   For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
3) Metallic nickel: (>99.9wt%, containing <0.005wt% Cr, Cu, Fe and <0.001wt% of Mn)
4) Metallic iron: (>99.9wt%, containing <0.005wt% Cr)
5) Molybdenum solution (10µg of Mo/m*l*): Dissolve 18.4g of 7-molybdic acid-6-ammonium-4-hydrate in about 600m*l* of warm water. After cooling to ambient temperature, transfer to a 1000m*l* volumetric flask using water, and bring up to volume with water. (Prepare each time)

Procedure:

1) The sample solution pretreated according to step a) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cr standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, weigh out 0.13g of metallic nickel and 0.010g of metallic iron, transfer these to several 200m*l* beakers, and perform the same operations as described in the pretreatment step a). Transfer each of these to a 100m*l* volumetric flask using water, and add 10m*l* of potassium disulfide solution (100g/*l*) and 6m*l* of molybdenum solution (10µg of Mo/m*l*). When the amount of Cr in the sample is 0.05 – 0.5%, add increasing volumes of Cr standard solution (100µg of Cr/m*l*) from 0 – 6.0m*l* (containing 0 – 600µg of Cr), or when the amount of Cr in the sample is 0. 5 – 2.0%, add increasing volumes of Cr standard solution (500µg of Cr/m*l*) from 0 – 4.0m*l* (containing 0 – 2000µg of Cr), and bring up to volume with water.

Note: For nickel-lead alloy cast metal, add the same amount of nickel and lead as contained in the weighed sample.

Measurement:

Measurement wavelength : 357.9nm

Calibration curve range : 0.5 – 20µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 13)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Cu

  Reagents:

  1) Cu standard solution (100µg of Cu/m*l*)
  2) Cu standard solution (500µg of Cu/m*l*)

     For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
  3) Metallic nickel: Same as for Cr, Reagent, 3)

  Procedure:

  1) The sample solution pretreated according to step b) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions used in generating the calibration curve, weigh out 0.20g of metallic nickel, transfer to each of several 200m*l* beakers, and perform the same operations as described in the pretreatment step b). Transfer each of these to a 100m*l* volumetric flask using water. When the amount of Cu in the sample is 0.05 – 0.5%, add increasing volumes of Cu standard solution (100µg of Cu/m*l*) from 0 – 6.0m*l* (containing 0 – 600µg of Cu), or when the amount of Cu in the sample is 0. 5 – 2.0%, add increasing volumes of Cu standard solution (500µg of Cu/m*l*) from 0 – 4.0m*l* (containing 0 – 2000µg of Cu), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 324.8nm
  Calibration curve range : 0.5 – 20µg /m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

  Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

  Reagents:

  1) Fe standard solution (100µg of Fe/m*l*)
  2) Fe standard solution (500µg of Fe/m*l*)

     For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
  3) Metallic nickel: Same as for Cr, Reagent, 3)

  Procedure:

  1) The sample solution pretreated according to step b) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve,

prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions used in generating the calibration curve, weigh out 0.20g of metallic nickel, transfer to each of several 200m*l* beakers, and perform the same operations as described in the pretreatment step b). Transfer each of these to a 100m*l* volumetric flask using water. When the amount of Fe in the sample is 0.05 – 0.5%, add increasing volumes of Fe standard solution (100µg of Fe/m*l*) from 0 – 6.0m*l* (containing 0 – 600µg of Fe). When the amount of Fe in the sample is 0. 5 – 2.0%, add increasing volumes of Fe standard solution (500µg of Fe/m*l*) from 0 – 4.0m*l* (containing 0 – 2000µg of Fe), and bring up to volume with water.

Note: For nickel-lead alloy cast metal, add the same amount of nickel and lead as contained in the weighed sample.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.5 – 20µg /m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 17)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Mn

Reagents:

1) Mn standard solution (100µg of Mn/m*l*)
2) Mn standard solution (500µg of Mn/m*l*)
   For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
3) Metallic nickel: Same as for Cr, Reagent, 3)

Procedure:

1) The sample solution pretreated according to step b) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mn standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions used in generating the calibration curve, weigh out 0.20g of metallic nickel, transfer to each of several 200m*l* beakers, and perform the same operations as described in the pretreatment step b). Transfer each of these to a 100m*l* volumetric flask using water. When the amount of Mn in the sample is 0.05 – 0.3%, add increasing volumes of Mn standard solution (100µg of Mn/m*l*) from 0 – 3.0m*l*

(containing 0 – 300µg of Mn). When the amount of Mn in the sample is 0.3 – 2.0%, add increasing volumes of Mn standard solution (500µg of Mn/m*l*) from 0 – 4.0m*l* (containing 0 – 200µg of Mn), and bring up to volume with water.

Note: For nickel-lead alloy cast metal, add the same amount of nickel and lead as contained in the weighed sample.

Measurement:

Measurement wavelength : 279.5nm

Calibration curve range : 0.2 – 20µg /m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 22)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

## 15.8 Analysis Method for Nickel Material for Electron Tubes

Reference materials: Japan Industrial Standard

| | |
|---|---|
| Quantitation Method for Magnesium in Nickel Material for Electron Tubes | JIS H 1423 |
| Quantitation Method for Lead in Nickel Material for Electron Tubes | JIS H 1424 |
| Quantitation Method for Iron in Nickel Material for Electron Tubes | JIS H 1425 |
| Quantitation Method for Manganese in Nickel Material for Electron Tubes | JIS H 1426 |
| Quantitation Method for Cobalt in Nickel Material for Electron Tubes | JIS H 1431 |

### 15.8.1 Sample Pretreatment

a) Co, Cu, Fe, Mn

- Sample weights

Weigh out the sample according to the amount of target element, referring to the table below.

| Element | Percent contained (%) | Weight (g) | Nitric Acid (1+1) Volume added (m*l*) |
|---|---|---|---|
| Co | 0.01 – 0.05 | 1.00 | 20 |
| | 0.05 – 0.50 | 0.10 | 20 |
| Cu | 0.005 – 0.01 | 5.00 | 50 |
| | 0.01 – 0.10 | 0.50 | 20 |
| | 0.01 – 0.20 | 0.20 | 20 |
| Fe | 0.01 – 0.05 | 1.00 | 20 |
| | 0.05 – 0.20 | 0.20 | 20 |
| Mn | 0.005 – 0.01 | 5.00 | 50 |
| | 0.01 – 0.10 | 0.50 | 20 |
| | 0.10 – 0.40 | 0.10 | 20 |

- Preparing sample solutions

Weigh out the sample, transfer to a 300m*l* beaker, cover with a watch glass, and add nitric acid (1+1). After heating gently to decompose, boil to drive off the nitrogen oxide. After cooling, transfer to a 100m*l* volumetric flask and bring up to volume with water.

b) Mg

- Sample weights

Weigh out the sample according to the amount of target element, referring to the table below.

| Percent contained (%) | Weight (g) | Nitric Acid (1+1) Volume added (m*l*) |
|---|---|---|
| 0.002 ☐ 0.01 | 1.00 | 20 |
| 0.01 ☐ 0.05 | 0.20 | 20 |
| 0.05 ☐ 0.2 | 0.10 | 20 |

- Preparing sample solutions

Weigh out the sample, transfer to a 300m*l* beaker, cover with a watch glass, and add nitric acid (1+1). After heating gently to decompose, boil to drive off the nitrogen oxide. After cooling, transfer to a 100m*l* volumetric flask, add 5m*l* of strontium solution (10mg of Sr/m*l*), and bring up to volume with water.

Note: Strontium solution (10mg of Sr/m*l*): Dissolve 30.4g of strontium chloride (6-hydrate) in water, transfer to a 1000m*l* volumetric flask, and bring up to volume with water.

15.8.2 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent contained (%) |
|---|---|
| Co | 0.01 – 0.50 |
| Cu | 0.005 – 0.20 |
| Fe | 0.01 – 0.20 |
| Mg | 0.002 – 0.20 |
| Mn | 0.005 – 0.40 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Co

  Reagents:

  1) Co standard solution (100µg of Co/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Metallic nickel: >99.9 %, containing little Co, Cu, Fe, Mg, Mn

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Co standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For standard solutions used in generating a calibration curve, weigh out the same amount of metallic nickel as the sample weight used, and transfer to each of several 300m*l* beakers. After performing the same heating procedure as for the sample to decompose, add increasing volumes of Co standard solution (100µg of Co/m*l*) from 0 – 5.0m*l* (containing 0 – 500µg of Co). After cooling, transfer to 100m*l* volumetric flasks, and bring up to volume with water.

  Measurement:

  Measurement wavelength : 240.7nm
  Calibration curve range : 0.5 – 5µg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 12)

- Cu

  Reagents:

  1) Cu standard solution (100µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Metallic nickel: Same as for Co, Reagent, 2)

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For standard solutions used in generating a calibration curve, weigh out the same amount of metallic nickel as the sample weight used, and transfer to each of several 300m*l* beakers. After performing the same heating procedure as for the sample to decompose, add increasing volumes of Cu standard solution (100µg of Cu/m*l*) from 0 – 5.0m*l* (containing 0 – 500µg of Cu). After cooling, transfer to 100m*l* volumetric

flasks, and bring up to volume with water.

Measurement:

Measurement wavelength : 324.8nm

Calibration curve range : 0.2 – 5µg/m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

Reagents:

1) Fe standard solution (100µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Metallic nickel: Same as for Co, Reagent, 2)

Procedure:

1) The sample solution pretreated according to step a) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, weigh out the same amount of metallic nickel as the sample weight used, and transfer to each of several 300m*l* beakers. After performing the same heating procedure as for the sample to decompose, add increasing volumes of Fe standard solution (100µg of Fe/m*l*) from 0 – 5.0m*l* (containing 0 – 500µg of Fe. After cooling, transfer to 100m*l* volumetric flasks, and bring up to volume with water.

Measurement:

Measurement wavelength : 248.3nm

Calibration curve range : 0.5 – 5µg/m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 17)

- Mg

Reagents:

1) Mg standard solution (20µg of Mg/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Metallic nickel: Same as for Co, Reagent, 2)
3) Sr solution (10mg of Sr/m*l*): Same as describe in NOTE for Sample Pretreatment, b)

Procedure:

1) The sample solution pretreated according to step b) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mg standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, weigh out the same amount of metallic nickel as the sample weight used, and transfer to each of several 300m*l* beakers. After performing the same heating procedure as for the sample to decompose, add increasing volumes of Mg standard solution (20µg of Mg/m*l*) from 0 – 10.0m*l* (containing 0 – 200µg of Mg). After cooling, transfer to 100m*l* volumetric flasks. Add 5m*l* of Sr solution (10mg of Sr/m*l*) to each flask, and bring up to volume with water.

Measurement:

Measurement wavelength : 285.2nm
Calibration curve range : 0.1 – 2µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 21)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Mn

Reagents:

1) Mn standard solution (100µg of Mn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Metallic nickel: Same as for Co, Reagent, 2)

Procedure:

1) The sample solution pretreated according to step a) is measured as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mn standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, weigh out the same amount of metallic nickel as the sample weight used, and transfer to each of several 300m*l* beakers. After performing the same heating procedure as for the sample to decompose, add increasing volumes of Mn standard solution (100µg of Mn/m*l*) from 0 – 5.0m*l* (containing 0 – 500µg of Mn). After cooling, transfer to 100m*l* volumetric flasks, and bring up to volume with water.

Measurement:

Measurement wavelength : 279.5nm
Calibration curve range : 0.2 – 5μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 22)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

## 15.9 Nickel Ore Analysis Method

Reference materials:

Japan Industrial Standard, Nickel Ore Analysis Method JIS H 1151

### 15.9.1 Sample Pretreatment

a) Co, Cu, Fe, Mn

Weigh out 5.0g of sample to the nearest 10mg and transfer to a 300m*l* beaker. Cover with a watch glass, add 40m*l* of nitric acid (1+1). Heat gently until decomposition is complete, and then boil until the nitrogen oxide is driven off. After cooling to ambient temperature, rinse the bottom of the watch glass with water and remove the watch glass. Transfer this solution to a 100m*l* volumetric flask using water, and bring up to volume with water.

b) Pb

Weigh out 5.0g of sample to the nearest 10mg and transfer to a 500m*l* beaker. Cover with a watch glass, add 40m*l* of nitric acid (1+1). Heat gently until decomposition is complete, and then boil until the nitrogen oxide is driven off. After cooling, rinse the bottom of the watch glass with water, remove the watch glass, and add water to a total volume of about 150m*l*.

Add 5m*l* of iron (III) solution, and while mixing this solution, little by little add 20m*l* of aqueous ammonia, then add 50m*l* more. Next, add about 15g of ammonium carbonate and dissolve. Heat and boil for about 5 minutes, and then let stand for 1 – 2 hours at 60 – 80°C. Filter out the precipitate using Type 5A filter paper, and rinse several times using warm ammonium rinse solution. Discard the rinse liquid and filtrate.

Using warm water, rinse the precipitate on the filter paper back into the original beaker. Place the beaker under the funnel, and drip 10m*l* of a nitric acid mixture onto the filter paper to dissolve any remaining precipitate on the filter paper and in the beaker. Then rinse the filter paper thoroughly with warm hydrochloric acid (1+50). Heat the solution until nearly evaporated. Add 5m*l* of hydrochloric acid (1+1) and 5m*l* of water, then heat to dissolve the salts. After cooling to ambient temperature, transfer to a 25m*l* volumetric flask, and bring up to volume with water.

Note:

1) Iron (III) solution: Dissolve 0.50g of iron (≥99.9%) in 20m*l* of hydrochloric acid (1+1) and

2m*l* of hydrogen peroxide, heat to completely dissolve and continue heating to drive off hydrogen peroxide. After cooling to ambient temperature, dilute to 100m*l* using water (Fe 5µg/m*l*).

2) Ammonia rinse solution: Dissolve 15g of ammonium carbonate in 500m*l* of aqueous ammonia (2+50).

### 15.9.2 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Co | 0.001 – 0.50 |
| Cu | 0.0005 – 0.50 |
| Fe | 0.0005 – 1.0 |
| Mn | 0.0001 – 0.004 |
| Pb | 0.0002 – 0.01 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Co

Reagents:

1) Co standard solution (50µg of Co/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Nickel: >99.9wt%, with known amount of Co, and amount of Co less than that in the sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 0.01 % of Co, the solution is measured as it is. If the solution contains more than 0.01 % of Co, use an aliquot having a Co concentration, which is within the calibration curve concentration range.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Co standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating a calibration curve, weigh out 5.0g of nickel,

and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, add increasing volumes of Co standard solution (50µg of Co/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Co), and bring up to volume with water.

If an aliquot of the sample solution is used, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, and bring up to volume with water. From this solution, take aliquots, each of which are equivalent in volume to the original aliquot taken from the sample solution, and transfer these to several 100m*l* volumetric flasks. Add increasing volumes of Co standard solution (50µg of Co/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Co), and bring up to volume with water.

Measurement:

Measurement wavelength : 240.7nm
Calibration curve range : 0.5 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 12)

- Cu

Reagents:

1) Cu standard solution (50µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Nickel: >99.9 %, with known amount of Cu, and amount of Cu less than that in the sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 0.01 % of Cu, the solution is measured as it is. If the solution contains more than 0.01 % of Cu, use an aliquot having a Cu concentration, which is within the calibration curve concentration range.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, add increasing volumes of Cu standard solution (50µg of Cu/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Cu), and bring up to volume with water.

If an aliquot of the sample solution is used, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, and bring up to volume with water. From this solution, take aliquots, each of which are equivalent in volume to the original aliquot taken from the sample solution, and transfer these to several 100m*l* volumetric flasks. Add increasing volumes of Cu standard solution (50µg of Cu/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Cu), and bring up to volume with water.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.2 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

Reagents:

1) Fe standard solution (50µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Nickel: >99.9wt%, with known amount of Fe, and amount of Fe less than that in the sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 0.01 % of Fe, the solution is measured as it is. If the solution contains more than 0.01 % of Fe, use an aliquot having a Fe concentration, which is within the calibration curve concentration range.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating a calibration curve, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, add increasing volumes of Fe standard solution (50µg of Fe/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Fe), and bring up to volume with water.

   If an aliquot of the sample solution is used, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, and bring up to volume with water. From this solution, take aliquots, each of which are equivalent in volume to the original aliquot taken from the sample solution, and transfer these to several 100m*l* volumetric flasks. Add increasing volumes of Fe standard solution (50µg of Fe/m*l*) from 0 – 10.0m*l* (containing 0 – 500µg of Fe), and bring up to volume with water.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.2 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- Mn

Reagents:

1) Mn standard solution (20µg of Mn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Nickel: >99.9wt%, with known amount of Mn, and amount of Mn less than that in the sample.

Procedure:

1) The sample solution pretreated according to step a) is measured as it is.
   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Mn standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, weigh out 5.0g of nickel, and transfer to each of several 300m*l* beakers. After performing the same procedure as for pretreatment of the sample using step a), transfer to 100m*l* volumetric flasks using water, add increasing volumes of Mn standard solution (20µg of Mn/m*l*) from 0 – 10.0m*l* (containing 0 – 200µg of Mn), and bring up to volume with water.

Measurement:

Measurement wavelength : 279.5nm
Calibration curve range : 0.05 – 2µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 22)

- Pb

Reagents:

1) Pb standard solution (50µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

2) Iron (III) solution: Prepared as described in the NOTE for Sample Pretreatment, b) Pb

Procedure:

1) The sample solution pretreated according to step b) is measured as it is.
   For blank measurement, perform the same pretreatment on the reagent containing no sample as that performed on the sample. This solution is measured, and the value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating a calibration curve, transfer increasing volumes of Pb standard solution (50μg of Pb/m*l*) from 0 – 10.0m*l* (containing 0 – 500μg of Pb) to several 25m*l* volumetric flasks. To each of these, add 5m*l* of iron (III) solution and 5m*l* of hydrochloric acid (1+1), and bring up to volume with water.

Measurement:

Measurement wavelength : 217.0nm
Calibration curve range : 0.4 – 20μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 26)

## 15.10 Lead Ore Analysis Method

Reference Materials:

Japan Industrial Standard, Lead Ore Analysis Method JIS H 1121

### 15.10.1 Sample Pretreatment

Weigh out 5.0g of sample to the nearest 10mg, and transfer to a 300m*l* beaker. Cover with at watch glass, add 10m*l* of tartaric acid solution (500 g/*l*) and 35m*l* of nitric acid (1+4). After heating gently to decompose, boil to drive off the nitrogen oxide. After cooling to ambient temperature, rinse the bottom surface of the watch glass and remove the watch glass. Transfer the solution to a 100m*l* volumetric flask using water, and bring up to volume with water.

### 15.10.2 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Ag | 0.0002 – 0.004 |
| Bi | 0.001 – 0.15 |
| Cu | 0.0005 – 0.05 |
| Fe | 0.0005 – 0.05 |
| Sb | 0.002 – 0.15 |
| Zn | 0.0005 – 0.015 |

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions.

- Ag

  Reagents:

  1) Ag standard solution (20µg of Ag/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Lead: >99.99 %, containing no Ag, or if present, with known amount of Ag, and containing less than that in the sample.

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is.
     For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Ag standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For standard solutions used in generating a calibration curve, weigh out several 5.0g portions of lead, and after performing the same procedure as that in pretreatment of the sample, transfer these to 100m*l* volumetric flasks using water. Add increasing volumes of Ag standard solution (20µg of Ag/m*l*) from 0 – 10.0m*l* (containing 0 – 200µg of Ag), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 328.1nm
  Calibration curve range : 0.1 – 2µg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 1)

- Bi

  Reagents:

  1) Bi standard solution (200µg of Bi/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Lead: >99.99 %, containing no Bi, or if present, with known amount of Bi, and containing less than that in the sample.

  Procedure:

  1) When the pretreated sample solution contains 0.001 – 0.06 % of Bi, it can be measured as it is. If it contains 0.06 – 0.15 %, take an exactly 20m*l* aliquot from the sample solution and transfer it to a 50m*l* volumetric flask. Add 3m*l* of tartaric acid solution (500 g/*l*) and 10m*l* of nitric acid (1+4), and bring up to volume with water.
     For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Bi standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating the calibration curve, if the Bi content is 0.001 – 0.06 %, weigh out several 5.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. Add increasing volumes of Bi standard solution (200µg of Bi/m*l*) from 0 – 15.0m*l* (containing 0 – 3000µg of Bi), bring up to volume with water, and use these solutions for measurement.

   If the Bi content is 0.06 – 0.15 %, weigh out several 2.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. The rest of the procedure is the same as that used when the Bi content is 0.001 – 0.06 %.

Measurement:

Measurement wavelength : 223.1nm
Calibration curve range : 0.5 – 3µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 8)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Cu

Reagents:

1) Cu standard solution (100µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Lead: >99.99 %, containing no Cu, or if present, with known amount of Cu, and containing less than that in the sample.

Procedure:

1) When the pretreated sample solution contains 0.0005 – 0.02 % of Cu, it can be measured as it is. If it contains 0.02 – 0.05 %, accurately take a 20m*l* aliquot from the sample solution and transfer it to a 50m*l* volumetric flask. Add 3m*l* of tartaric acid solution (500 g/*l*) and 10m*l* of nitric acid (1+4), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating the calibration curve, if the Cu content is 0.0005 – 0.02 %, weigh out several 5.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. Add increasing volumes of Cu standard solution (100µg of Cu/m*l*)

from

0 – 10.0m*l* (containing 0 – 1000μg of Cu), bring up to volume with water, and use these solutions for measurement.

If the Cu content is 0.02 – 0.05 %, weigh out several 2.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. The rest of the procedure is the same as that used when the Cu content is 0.0005 – 0.02 %.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.2 – 10μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Fe

Reagents:

1) Fe standard solution (100μg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Lead: >99.99 %, containing no Fe, or if present, with known amount of Fe, and containing less than that in the sample.

Procedure:

1) When the pretreated sample solution contains 0.0005 – 0.02 % of Fe, it can be measured as it is. If it contains 0.02 – 0.05 %, accurately take a 20m*l* aliquot from the sample solution and transfer it to a 50m*l* volumetric flask. Add 3m*l* of tartaric acid solution (500 g/*l*) and 10m*l* of nitric acid (1+4), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating the calibration curve, if the Fe content is 0.0005 – 0.02 %, weigh out several 5.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. Add increasing volumes of Fe standard solution (100μg of Fe/m*l*) from 0 – 10.0m*l* (containing 0 – 1000μg of Fe), bring up to volume with water, and use these solutions for measurement.

   If the Fe content is 0.02 – 0.05 %, weigh out several 2.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. The rest of the procedure is the same as that used when the Fe content is 0.0005 – 0.02 %.

Measurement:

Measurement wavelength : 248.3nm

Calibration curve range : 0.2 – 10µg/m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

- Sb

Reagents:

1) Sb standard solution (200µg of Sb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Lead: >99.99 %, containing no antimony, or if present, with known amount of antimony, and containing less than that in the sample.

Procedure:

1) When the pretreated sample solution contains 0.002 – 0.06 % of Sb, it can be measured as it is. If it contains 0.06 – 0.15 %, accurately take a 20m*l* aliquot from the sample solution and transfer it to a 50m*l* volumetric flask. Add 3m*l* of tartaric acid solution (500 g/*l*) and 10m*l* of nitric acid (1+4), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Sb standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For standard solutions used in generating the calibration curve, if the Sb content is 0.002 – 0.06 %, weigh out several 5.0g portions of lead and perform the same pretreatment as that used for the sample. Transfer these to several 100m*l* volumetric flasks using water. Add increasing volumes of Sb standard solution (200µg of Sb/m*l*) from

   0 – 15.0m*l* (containing 0 – 3000µg of Sb), bring up to volume with water, and use these solutions for measurement.

   If the Sb content is 0.06 – 0.15 %, weigh out several 2.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. The rest of the procedure is the same as that used when the Sb content is 0.002 – 0.06 %.

Measurement:

Measurement wavelength : 217.6nm

Calibration curve range : 1 – 30µg/m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 32)

- Zn

Reagents:

1) Zn standard solution (20µg of Zn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Lead: >99.99 %, containing no zinc, or if present, with known amount of zinc, and containing less than that in the sample.

Procedure:

1) When the pretreated sample solution contains 0.0005 – 0.006 % of Zn, it can be measured as it is. If it contains 0.006 – 0.015 %, take an exactly 20m*l* aliquot from the sample solution and transfer it to a 50m*l* volumetric flask. Add 3m*l* of tartaric acid solution (500 g/*l*) and 10m*l* of nitric acid (1+4), and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Zn standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For standard solutions used in generating the calibration curve, if the Zn content is 0.0005 – 0.006 %, weigh out several 5.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. Add increasing volumes of Zn standard solution (20µg of Zn/m*l*) from 0 – 15.0m*l* (containing 0 – 300µg of Zn), bring up to volume with water, and use these solutions for measurement.

   If the Zn content is 0.006 – 0.015 %, weigh out several 2.0g portions of lead, perform the same pretreatment as that used for the sample, and transfer these to several 100m*l* volumetric flasks using water. The rest of the procedure is the same as that used when the Zn content is 0.0005 – 0.006 %.

Measurement:

Measurement wavelength : 213.9nm

Calibration curve range : 0.2 – 3µg/m*l*

Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 44)

Note: If the standard solution absorbance exceeds 0.5, adjust the burner angle so that an absorbance of 0.5 is obtained for the standard solution with the highest concentration.

## 15.11 Tin Ore Analysis Method

Reference Materials:

Japan Industrial Standard, Tin Ore Analysis Method JIS H 1141

### 15.11.1 Sample Pretreatment

a) Direct method

Weigh out 1.00g of sample to the nearest 1mg and transfer to a 200m*l* beaker. Cover with a watch glass, little by little add 20m*l* of acid mixture (3 parts hydrochloric acid, 1 part nitric acid) to decompose. After the intense reaction subsides, heat gently until decomposition is complete. After cooling to ambient temperature, rinse the bottom surface of the watch glass and remove the watch glass. Transfer the solution to a 100m*l* volumetric flask using water, and bring up to volume with water.

b) Tin separation method

Weigh out 2.00g of sample to the nearest 1mg and transfer to a 200m*l* beaker. Cover with a watch glass, little by little add 10m*l* of acid mixture (3 parts hydrochloric acid, 1 part nitric acid) to decompose. After the intense reaction subsides, heat gently until decomposition is complete. After cooling, rinse the bottom surface of the watch glass and remove the watch glass. Add 10m*l* of sulfuric acid (1+1), and heat until volatilization of the white fumes of sulfuric acid occurs. After allowing to cool for several minutes, add 20m*l* of hydrobromic acid, and heat until thick white fumes are generated. After allowing to cool for several minutes, add 10m*l* of hydrobromic acid, and heat again until thick white fumes are generated. After cooling to ambient temperature, transfer the solution to a 25m*l* volumetric flask using water, and bring up to volume with water.

### 15.11.2 Electrical Heating Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| As | 0.0003 – 0.01 (Direct method) |
| Sb | 0.0003 – 0.01 (Direct method) |

Note: If the high purity tin mentioned in the next section cannot be obtained, this method is not applicable.

b) Measurement procedure

Measurement is conducted using the following procedure. For the lamp current and slit width, refer to Cookbook Section 4, Item 7.5 Element Specific Measurement Conditions.

- As

Reagents:

1) As standard solution (0.5μg of As/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Tin: High purity tin (>99.999 %), containing <0.00003 % arsenic

Procedures:

1) When the sample solution pretreated according to step a) contains less than 0.001 % of As, transfer a 50m*l* aliquot from the sample solution to a 100m*l* volumetric flask and bring up to volume with water. If the sample solution contains more than 0.001 %, transfer a 5.0m*l* aliquot from the sample solution to a 100m*l* volumetric flask and bring up to volume with water.

   When preparing the standards for generating the calibration curve, prepare and measure prepare and measure a solution containing no added As standard solution for blank measurement. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used for generating the calibration curve, when the amount of As in the sample is less than 0.001 %, weigh out several 1.00g portions of tin and transfer these to separate 200m*l* beakers. For each of these, perform the pretreatment procedure a) just as that for the sample, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water. Transfer exactly 50m*l* aliquots from each of these solutions to several 100m*l* volumetric flasks. Add increasing volumes of the As standard solution (0.5μg of As/m*l*) from 0 – 10.0m*l* (As content from 0 – 5μg), and bring up to volume with water.

   When the amount of As in the sample is more than 0.001 %, weigh out several 1.00g portions of tin and transfer these to separate 200m*l* beakers. For each of these, perform the pretreatment procedure a) just as that for the sample, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water. Transfer exactly 5.0m*l* aliquots from each of these solutions to several 100m*l* volumetric flasks. Add increasing volumes of the As standard solution (0.5μg of As/m*l*) from 0 – 10.0m*l* (As content from 0 – 5μg), and bring up to volume with water.

Measurement:

| | |
|---|---|
| Measurement wavelength | : 193.7nm |
| Calibration curve range | : 2 – 50 ng/m*l* |
| Tube | : High density graphite tube |
| Sample injection volume | : 20μ*l* |

Heating conditions :

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 400 | 10 | R | 1.0 |
| 4 | 400 | 20 | S | 1.0 |
| 5 | 400 | 3 | S | 0.0 |
| 6 | 2200 | 3 | S | 0.0 |
| 7 | 2500 | 2 | S | 1.0 |

- Sb

Reagents:

1) Sb standard solution (0.5µg of Sb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards.
2) Tin: High purity tin (>99.999 %), containing <0.00003 % antimony

Procedures:

1) When the sample solution pretreated according to step a) contains less than 0.001 % of Sb, transfer a 50m*l* aliquot from the sample solution to a 100m*l* volumetric flask and bring up to volume with water. If the sample solution contains more than 0.001 %, transfer a 5.0m*l* aliquot from the sample solution to a 100m*l* volumetric flask and bring up to volume with water.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Sb standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, when the amount of Sb in the sample is less than 0.001 %, weigh out several 1.00g portions of tin and transfer these to separate 200m*l* beakers. For each of these, perform the pretreatment procedure a) just as that for the sample, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water. Transfer exactly 50m*l* aliquots from each of these solutions to several 100m*l* volumetric flasks. Add increasing volumes of the Sb standard solution (0.5µg of Sb/m*l*) from 0 – 10.0m*l* (Sb content from 0 – 5µg), and bring up to volume with water.

   When the amount of Sb in the sample is more than 0.001 %, weigh out several 1.00g portions of tin and transfer these to separate 200m*l* beakers. For each of these, perform the pretreatment procedure a) just as that for the sample, transfer to a 100m*l* volumetric flask using water, and bring up to volume with water. Transfer exactly 5.0m*l* aliquots from each of these solutions to several 100m*l* volumetric flasks. Add increasing volumes of the Sb standard solution (0.5µg of Sb/m*l*) from 0 – 10.0m*l* (Sb content from 0 – 5µg), and bring up to volume with water.

Measurement:

Measurement wavelength : 217.6nm
Calibration curve range : 5 – 50 ng/m*l*
Tube : Pyrolized graphite tube
Sample injection volume : 20µ*l*
Heating conditions :

| | TEMP (□Ž) | TIME (sec) | HEAT | GAS (*l*/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 400 | 10 | R | 1.0 |
| 4 | 400 | 20 | S | 1.0 |
| 5 | 400 | 3 | S | 0.0 |
| 6 | 2200 | 3 | S | 0.0 |
| 7 | 2500 | 2 | S | 1.0 |

### 15.11.3 Flame Atomic Absorption Method

a) Target elements and quantitation range

| Element | Percent contained (%) |
|---|---|
| Cu | 0.001 – 0.05 (Direct method) |
| | 0.0001 – 0.005 (Tin separation method) |
| Fe | 0.001 – 0.05 (Direct method) |
| | 0.0003 – 0.005 (Tin separation method) |
| Pb | 0.002 – 0.10 (Direct method) |
| | 0.0002 – 0.01 (Tin separation method) |

Note: If the high purity tin mentioned in the next section cannot be obtained, this method is not applicable.

b) Measurement procedure

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

- Cu I (Direct method)

  Reagents:

  1) Cu standard solution (20μg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Tin: >99.99 %, with known amount of Cu, and containing less than that in the sample.

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is.

     For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.00g portions of tin and transfer to separate 200m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, and add increasing volumes of the Cu standard solution (20μg of Cu/m*l*) from 0 – 25.0m*l* (Cu content from 0 – 500μg), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 324.8nm
  Calibration curve range : 0.1 – 5μg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

- Cu II (Tin separation method)

  Reagents:

  1) Cu standard solution (10μg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

  Procedure:

  1) The sample solution pretreated according to step b) is measured as it is.

     For blank measurement, reagent containing no sample is pretreated using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Cu standard solution (10μg of Cu/m*l*) from 0 – 10.0m*l* (Cu content from 0 – 100μg) to several 25m*l* volumetric flasks, add 10m*l* of nitric acid (1+2) and bring up to volume with water.

Measurement: Same as for Cu I

- Fe I (Direct method)

  Reagents:

  1) Fe standard solution (20µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Tin: >99.99 %, with known amount of Fe, and containing less than that in the sample.

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is.

     For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.00g portions of tin and transfer to separate 200m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, and add increasing volumes of the Fe standard solution (20µg of Fe/m*l*) from 0 – 25.0m*l* (Fe content from 0 – 500µg), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 248.3nm
  Calibration curve range : 0.1 – 5µg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- Fe II (Tin separation method)

  Reagents:

  Fe standard solution (10µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

  Procedure:

  1) The sample solution pretreated according to step b) is measured as it is.

     Pre-treat reagent containing no sample using the same procedure as that used for the sample for blank measurement. After measurement, the value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Fe standard solution (10µg of Fe/m*l*) from 0 – 10.0m*l* (Fe content from 0 – 100µg) to several 25m*l* volumetric flasks, add 10m*l* of nitric acid (1+2) and bring up to volume with water.

Measurement: Same as for Fe I

- Pb I (Direct method)

  Reagents:

  1) Pb standard solution (100µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Tin: >99.99 %, with known amount of Pb, and containing less than that in the sample.

  Procedure:

  1) The sample solution pretreated according to step a) is measured as it is.

     For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Pb standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.00g portions of tin and transfer to separate 200m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, and add increasing volumes of the Pb standard solution (100µg of Pb/m*l*) from 0 – 10.0m*l* (Pb content from 0 – 1000µg), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 217.0nm
  Calibration curve range : 0.2 – 10µg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 26)

- Pb II (Tin separation method)

  Reagents:

  Pb standard solution (20µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

  Procedure:

  1) The sample solution pretreated according to step b) is measured as it is.

     For blank measurement, reagent containing no sample is pretreated using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Pb standard solution (20µg of Pb/m*l*) from 0 – 10.0m*l* (Pb content from 0 – 200µg) to several 25m*l* volumetric flasks, add 10m*l* of nitric acid (1+2) and bring up to volume with water.

  Measurement: Same as for Pb I

## 15.12 Cadmium Ore Analysis Method

Reference Materials:

Japan Industrial Standard, Cadmium Ore Analysis Method JIS H 1161

### 15.12.1 Sample Pretreatment

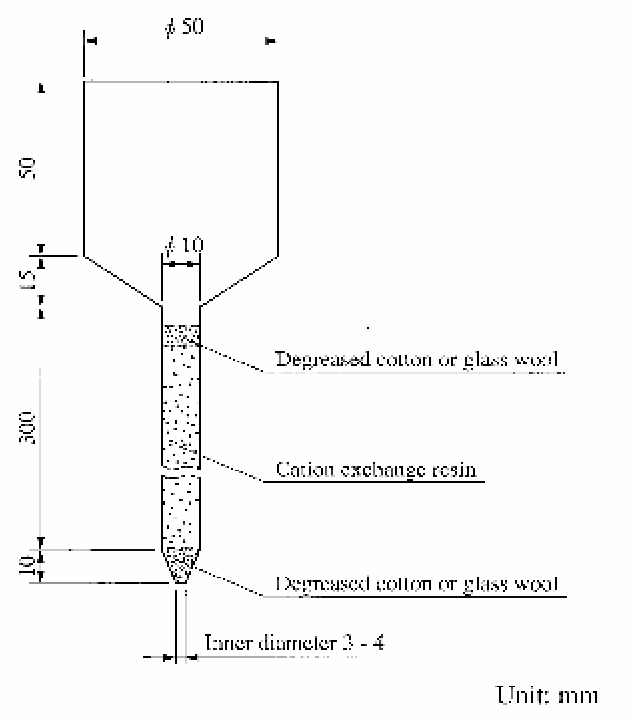
a) Direct method

Weigh out 5.0g of sample and transfer to a 300m*l* beaker. Cover with a watch glass, and add 50m*l* of nitric acid (1+3). After the intense reaction subsides, rinse the bottom surface of the watch glass and remove the watch glass. Transfer this solution to a 100m*l* volumetric flask and bring up to volume with water.

b) Ion exchange separation method

Weigh out 5.0g of sample and transfer to a 300m*l* beaker. Cover with a watch glass, add 40m*l* of acid mixture (10 parts hydrochloric acid, 2 parts nitric acid, 10 parts water). After the intense reaction subsides, heat gently until decomposition is complete. Continue heating until the solution is concentrated to a syrupy consistency. After cooling, rinse the bottom surface of the watch glass and remove the watch glass. Add 20m*l* of hydrochloric acid (1+1), heat until the salts are dissolved. Then cool to room temperature.

Prepare a caption exchange column as displayed in the following figure, and loosely pack in the bottom of the glass tube a 5 – 10mm thick layer of degreased cotton or glass wool. Pour onto this bed about 18m*l* of a water-swollen slurry of strongly acidic caption exchange resin (particle diameter 74 – 149µm, exchange capacity greater than 1.9 m equivalence/m*l*). After the resin settles, loosely pack on top of this a 5mm thick layer of degreased cotton or glass wool. Adjust the degreased cotton or glass wool so that the flow rate through the column is 1 – 2m*l*/min. Then pass through the column 50m*l* of sodium hydroxide solution (10g/*l*) and 50m*l* of water, in that order, and store the resin in NaR form.(R= an organic group)



**Caption Exchange Column Example**

Pass the solution, which has been cooled to room temperature, through the prepared caption exchange column. Next, rinse the interior wall of the beaker twice with 10m*l* of hydrochloric acid (1+16). After passing each of these rinses through the column, once again pass through 80m*l* of hydrochloric acid (1+16) to elute the cadmium. This elute may be discarded. Place the column over a 200m*l* receiving beaker and continue passing through the column 10m*l* of hydrochloric acid (1+3) to elute the lead. Heat the elute for about 10 minutes, then cool to ambient temperature, transfer to a 25m*l* volumetric flask, and bring up to volume with water.

Note:

1) Depending on the column used, the volume of hydrochloric acid (1+16) necessary to elute the cadmium may vary, so be sure to verify the elution curve, and if necessary, adjust the amount of acid used.
2) Depending on the column used, the volume of hydrochloric acid (1+3) necessary to elute the lead may vary, so be sure to verify the elution curve, and if necessary, adjust the amount of acid used.

15.12.2 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Cu | 0.0002 – 0.05 (Direct method) |

| | | |
|---|---|---|
| | 0.0001 – 0.005 | (Ion exchange separation method) |
| Fe | 0.0002 – 0.02 | (Direct method) |
| | 0.0001 – 0.002 | (Ion exchange separation method) |
| Pb | 0.0005 – 0.05 | (Direct method) |
| | 0.0001 – 0.01 | (Ion exchange separation method) |
| Zn | 0.0001 – 0.01 | (Direct method) |
| | 0.0001 – 0.001 | (Ion exchange separation method) |

Note: In the Direct method, if the high purity cadmium cannot be obtained, this method is not applicable.

b) Measurement procedure

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

- Cu I (Direct method)

Reagents:

1) Cu standard solution (20µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Cadmium: >99.99 %, with known amount of Cu, and containing less than that in the sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 500µg of Cu, the solution is measured as it is. When there is more than 500µg of Cu, transfer a 10.0m*l* aliquot from the sample solution to a 50m*l* volumetric flask. Add 5m*l* of nitric acid (1+1), and bring up to volume with water.
2) For the standard solutions to be used in generating the calibration curve, when there is less than 500µg of Cu, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water. Add increasing volumes of the Cu standard solution (20µg of Cu/m*l*) from 0 – 25.0m*l* (Cu content from 0 – 500µg), and bring up to volume with water.

   When there is more than 500µg of Cu, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, and bring up to volume with water. Transfer several 10.0m*l* aliquots from this solution to separate 50m*l* volumetric flasks. Add 5m*l* of nitric acid (1+1) and then add increasing volumes of the Cu standard solution (20µg of Cu/m*l*) from 0 – 12.5m*l* (Cu content from 0 – 250µg), and bring up to volume with water.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.1 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

- Cu II (Ion exchange separation method)

Reagents:

Cu standard solution (10µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) When the sample solution pretreated according to step b) contains less than 100µg of Cu, the solution is measured as it is. When there is more than 100µg of Cu, transfer a 10.0m*l* aliquot from the sample solution to a 25m*l* volumetric flask, and bring up to volume with water.

   For blank measurement, pre-treat reagent containing no sample using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Cu standard solution (10µg of Cu/m*l*) from 0 – 10.0m*l* (Cu content from 0 – 100µg) to several 25m*l* volumetric flasks. Add 10m*l* of hydrochloric acid (1+1) and bring up to volume with water.

Measurement: Same as for Cu I

- Fe I (Direct method)

Reagents:

1) Fe standard solution (20µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Cadmium: >99.99 %, with known amount of Fe, and containing less than that in the sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 500mg of Fe, the solution is measured as it is. When there is more than 500mg of Fe, transfer a 10.0m*l* aliquot from the sample solution to a 50m*l* volumetric flask. Add 5m*l* of nitric acid (1+1), and bring up to volume with water.

2) For the standard solutions to be used in generating the calibration curve, when there is less than 500µg of Fe, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, add increasing volumes of the Fe standard solution (20µg of Fe/m*l*) from 0 – 25.0m*l* (Fe content from 0 – 500µg), and bring up to volume with water.

   When there is more than 500µg of Fe, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, and bring up to volume with water. Transfer several 10.0m*l* aliquots from this solution to separate 50m*l* volumetric flasks. Add 5m*l* of nitric acid (1+1) and then add increasing volumes of the Fe standard solution (20µg of Fe/m*l*) from 0 – 10m*l* (Fe content from 0 – 200µg), and bring up to volume with water.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.1 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- Fe II (Ion exchange separation method)

Reagents:

Fe standard solution (10µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b is measured as it is.

   For blank measurement, reagent containing no sample is pretreated using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Fe standard solution (10µg of Fe/m*l*) from 0 – 10.0m*l* (Fe content from 0 – 100µg) to several 25m*l* volumetric flasks. Add 10m*l* of hydrochloric acid (1+1) and bring up to volume with water.

Measurement: Same as for Fe I

- Pb I (Direct method)

Reagents:

1) Pb standard solution (50µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Cadmium: >99.99 %, with known amount of Pb, and containing less than that in the

sample.

Procedure:

1) When the sample solution pretreated according to step a) contains less than 1000µg of Pb, the solution is measured as it is. When there is more than 1000µg of Pb, transfer a 10.0m*l* aliquot from the sample solution to a 50m*l* volumetric flask. Add 5m*l* of nitric acid (1+1), and bring up to volume with water.
2) For the standard solutions to be used in generating the calibration curve, when there is less than 1000µg of Pb, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, add increasing volumes of the Pb standard solution (50µg of Pb/m*l*) from 0 – 20.0m*l* (Pb content from 0 – 1000µg), and bring up to volume with water.

   When there is more than 1000µg of Pb, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as for the sample, described in step a), transfer to several 100m*l* volumetric flasks, and bring up to volume with water. Transfer several 10.0m*l* aliquots from this solution to separate 50m*l* volumetric flasks. Add 5m*l* of nitric acid (1+1) and then add increasing volumes of the Pb standard solution (50µg of Pb/m*l*) from 0 – 10.0m*l* (Pb content from 0 – 500µg), and bring up to volume with water.

Measurement:

Measurement wavelength: 217.0nm

Calibration curve range: 0.25 – 10µg/m*l*

Measurement conditions: Refer to Cookbook Section 3, Item 6.4, 26)

- Pb II (Ion exchange separation method)

Reagents:

Pb standard solution (25µg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) When the sample solution pretreated according to step b) contains less than 250µg of Pb, the solution is measured as it is. When there is more than 250µg of Pb, transfer a 10.0m*l* aliquot from the sample solution to a 25m*l* volumetric flask, and bring up to volume with water.

   For blank measurement, reagent containing no sample is pretreated using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, add increasing

volumes of the Pb standard solution (25µg of Pb/m*l*) from 0 – 10.0m*l* (Pb content from 0 – 250µg) to several 25m*l* volumetric flasks. Add 10m*l* of hydrochloric acid (1+1) and bring up to volume with water.

Measurement: Same as for Pb I

- Zn I (Direct method)

  Reagents:

  1) Zn standard solution (5µg of Zn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
  2) Cadmium: >99.99 %, with known amount of Zn, and containing less than that in the sample.

  Procedure:

  1) When the sample solution pretreated according to step a) contains less than 100µg of Zn, the solution is measured as it is. When there is more than 100µg of Zn, transfer a 10.0m*l* aliquot from the sample solution to a 50m*l* volumetric flask. Add 5m*l* of nitric acid (1+1), and bring up to volume with water.
  2) For the standard solutions to be used in generating the calibration curve, when there is less than 100µg of Zn, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks using water, add increasing volumes of the Zn standard solution (5µg of Zn/m*l*) from 0 – 20.0m*l* (Zn content from 0 – 100µg), and bring up to volume with water.

     When there is more than 100mg of Zn, weigh out several 5.0g portions of cadmium and transfer to separate 300m*l* beakers. After performing the same pretreatment procedure as that for the sample, described in step a), transfer to several 100m*l* volumetric flasks, and bring up to volume with water. Transfer several 10.0m*l* aliquots from this solution to separate 50m*l* volumetric flasks. Add 5m*l* of nitric acid (1+1) and then add increasing volumes of the Zn standard solution (5µg of Zn/m*l*) from 0 – 10.0m*l* (Zn content from 0 – 50µg), and bring up to volume with water.

  Measurement:

  Measurement wavelength : 213.9nm

  Calibration curve range : 0.05 – 1µg/m*l*

  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 44)

- Zn II (Ion exchange separation method)

  Reagents:

  Zn standard solution (2µg of Zn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing

Standards

Procedure:

1) When the sample solution pretreated according to step b) contains less than 20μg of Zn, the solution is measured as it is. When there is more than 20μg of Zn, transfer a 10.0m*l* aliquot from the sample solution to a 25m*l* volumetric flask, and bring up to volume with water.

   For blank measurement, reagent containing no sample is pretreated using the same procedure as that used for the sample. After measurement, the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, add increasing volumes of the Zn standard solution (2μg of Zn/m*l*) from 0 – 10.0m*l* (Zn content from 0 – 20μg) to several 25m*l* volumetric flasks. Add 10m*l* of hydrochloric acid (1+1) and bring up to volume with water.

Measurement: Same as for Zn I

## 15.13 Silver Ore Analysis Method

Reference Materials:

Japan Industrial Standard, Silver Ore Analysis Method JIS H1181

### 15.13.1 Sample Pretreatment

a) Bi, Pb

Weigh out 10g of sample, and transfer to a 300m*l* beaker. Cover with a watch glass, add 40m*l* of nitric acid, and heat gently to decompose. Add water to a volume of about 100m*l*. Add 5m*l* of ferric ammonium sulfate, and while mixing, add aqueous

ammonia. After the formation of iron hydroxide precipitate, add 20m*l* more of the aqueous ammonia. Next, add 5g of ammonium carbonate and heat. After boiling gently for about 10 minutes, set aside in a warm location (60 – 80°C) for 30 minutes. Separate the precipitate using Type 5A filter paper, and, after rinsing several times with warm ammonia rinse solution, transfer it to the original beaker by rinsing with warm water. Place the beaker under the filter, and drip 10m*l* of hydrochloric acid (1+1) over the filter paper to dissolve the precipitate on the filter paper and in the beaker. Rinse the filter paper thoroughly with warm water, and combine this liquid with that in the original beaker. Heat this solution to concentrate down to a volume of about 10m*l*.

Transfer the solution to a 100m*l* beaker using warm hydrochloric acid (1+50), add 2m*l* of sulfuric acid (1+1) and heat to concentrate until nearly evaporated. After cooling, add 5m*l* of hydrochloric acid (1+2), cover with a watch glass, heat to dissolve, and keep heating until nearly evaporated. After cooling once again, add 5m*l* of hydrochloric acid (1+2), cover with a watch glass, and heat to dissolve. After cooling, transfer to a 25m*l* volumetric flask using hydrochloric acid (1+50), and dilute up to volume.

Note:

1) Ferric ammonium sulfate: Dissolve 5g of ferric ammonium sulfate in nitric acid (1+100) and bring up to 100m*l*.
2) Ammonia rinse solution: Dissolve 5g of ammonium carbonate in 500m*l* of aqueous ammonia (1+19)

b) Cu, Fe

Weigh out 10g of sample, and transfer to a 500m*l* beaker. Cover with a watch glass, add 40m*l* of sulfuric acid (1+1), and heat gently to decompose. Add warm water to a volume of about 100m*l*. While mixing this solution, little by little add 20m*l* of hydrochloric acid (1+1) to precipitate out the silver chloride, and keep mixing for 10 minutes longer.

After cooling, pass the solution through Type 5B filter paper, and rinse several times with hydrochloric acid (1+100). To the filtrate and rinse solution, add 2m*l* of sulfuric acid (1+1), and heat until nearly evaporated. After cooling, add 5m*l* of hydrochloric acid (1+2), heat to dissolve, and evaporate to near dryness. After cooling, once again add 5m*l* of hydrochloric acid (1+2), cover with a watch glass, and heat to dissolve. After cooling, transfer to a 25m*l* volumetric flask and bring up to volume with water.

15.13.2 Flame Atomic Absorption Method

a) Target element and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Bi | >0.0001 |
| Cu | >0.0001 |
| Fe | >0.0002 |
| Pb | >0.0001 |

b) Measurement procedure

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

- Bi

Reagents:

1) Bi standard solution (10µg of Bi/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Ferric ammonium sulfate solution: Refer to NOTE 1) for Sample Pretreatment for a) Bi, Cu

Procedure:

1) The sample solution pretreated according to step a) is measured just as it is. When the percent content of Bi in the sample is high, use an aliquot from the 25m*l* sample solution, which contains 50 – 250µg of Bi, and use the same concentration of hydrochloric acid as the concentration of the sample.

   At this time, for a blank test, take an appropriate amount of reagent containing no sample, perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, transfer increasing volumes of Bi standard solution (10µg of Bi/m*l*) from 0 – 25.0m*l* (containing 0 – 250µg of Bi) to several 100m*l* beakers. Add 5m*l* of ferric ammonium sulfate solution and 2m*l* of sulfuric acid (1+1), and heat until evaporated. Then follow the procedure described in the Sample Pretreatment for a) Bi, Cu after "from the addition of 5m*l* of the hydrochloric acid (1+2)".

Measurement:

Measurement wavelength : 223.1nm
Calibration curve range : 1 – 10µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 8)

- Cu

Reagents:

Cu standard solution (10µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. When the percent content of Cu in the sample is high, use an aliquot from the 25m*l* of sample solution, which contains 25 – 100µg of Cu, and use the same concentration of chlorine as the concentration of the sample.

   For a blank test, take an appropriate amount of reagent containing no sample, perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, transfer increasing volumes of Cu standard solution (10µg of Cu/m*l*) from 0 – 10.0m*l* (containing 0 – 100µg of Cu) to several 25m*l* volumetric flasks. Add 6m*l* of hydrochloric acid (1+2) and bring up to volume with water.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.2 – 4μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

- Fe

Reagents:

Fe standard solution (10μg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. When the percent content of Fe in the sample is high, use an aliquot from the 25m*l* of sample solution, which contains 25 – 100μg of Fe, and use the same concentration of hydrochloric acid as the concentration of the sample.

   At this time, for a blank test, take an appropriate amount of reagent containing no sample, and perform the same pretreatment as that used for the sample. Then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, transfer increasing volumes of Fe standard solution (10μg of Fe/m*l*) from 0 – 10.0m*l* (containing 0 – 100μg of Fe) to several 25m*l* volumetric flasks. Add 6m*l* of hydrochloric acid (1+2) and bring up to volume with water.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.5 – 4μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- Pb

Reagents:

1) Pb standard solution (10μg of Pb/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Ferric ammonium sulfate solution: Refer to NOTE 1) for Sample Pretreatment for a) Bi, Cu

Procedure:

1) The sample solution pretreated according to step a) is measured just as it is. When the percent content of Pb in the sample is high, use an aliquot from the 25m*l* sample solution, which contains 50 – 250μg of Pb, and use the same concentration of

hydrochloric acid as the concentration of the sample.

At this time, for a blank test, take an appropriate amount of reagent containing no sample. Perform the same pretreatment as that used for the sample, and then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.

2) For the standard solutions used in generating the calibration curve, transfer increasing volumes of Pb standard solution (10μg of Pb/m*l*) from 0 – 25.0m*l* (containing 0 – 250μg of Pb) to several 100m*l* beakers. Add 5m*l* of ferric ammonium sulfate solution and 2m*l* of sulfuric acid (1+1), and heat until evaporated. Then follow the Sample Pretreatment procedure described above after "from the addition 5m*l* of the hydrochloric acid (1+2)......". Perform measurement using the resulting solution.

Measurement:

Measurement wavelength : 283.3nm
Calibration curve range : 1 – 10μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

## 15.14 Magnesium Ore Analysis Method

Reference Materials:

Japan Industrial Standard, Magnesium Ore Analysis Method JIS H 1321

### 15.14.1 Sample Pretreatment

Weigh out 1.0g of sample and transfer to a 300m*l* beaker. Add about 10m*l* of water, cover with watch glass, and little by little add 20m*l* of hydrochloric acid (1+1). When the reaction has subsided, add 1m*l* of hydrogen peroxide. Heat until decomposition is complete, and then cools. Transfer to a 100m*l* volumetric flask and bring up to volume with water.

### 15.14.2 Flame Atomic Absorption Method

a) Target elements and quantitation range

| Element | Percent Contained (%) |
|---|---|
| Cu | >0.0002 (DADDC - APDC extraction method) |
| Fe | >0.001 (DADDC - APDC extraction method) |
| Mn | 0.0005 – 0.02 |
| Ni | >0.0002 (DADDC - APDC extraction method) |
| Zn | 0.001 – 0.05 |

b) Measurement procedure

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

- Cu

Reagents:

1) Cu standard solution (5µg of Cu/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Tartaric acid solution (40 w/v%)
3) Diethyl ammonium diethyldithiocarbamate (DADDC) solution: Dissolve 0.5g of diethyl ammonium diethyldithiocarbamate in water, and dilute to 100m*l*. If there are impurities, filter and use the filtrate. (Prepare each time)
4) Ammonium pyrrolizidine dithiocarbamate (APDC) solution: Dissolve 0.5g of ammonium pyrrolizidine dithiocarbamate in water, and dilute to 100m*l*. If there are impurities, filter and use the filtrate.
5) n-butyl acetic acid
6) Methyl red solution: Dissolve 0.2g of methyl red in 90m*l* of ethanol, and dilute to 100m*l*.

Procedure:

1) Take an aliquot from the sample solution containing 5 – 20µg of Cu, and transfer to a 200m*l* beaker. Add 20m*l* of tartaric acid (40 w/v%), and dilute to about 80m*l* with water. Next, adjust to a pH of 5.8±0.2 using aqueous ammonia or hydrochloric acid solution. Transfer to a 200m*l* separating funnel, add water to bring volume to about 100m*l*, add 5m*l* of DADDC solution and 5m*l* of APDC solution and shake to mix. Add exactly 20m*l* of n-butyl acetic acid, shake vigorously for 3 minutes. After the contents separate into 2 layers, dehydrate the organic phase and use for measurement.

   For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.

   Note: For the dehydration procedure, pack dry filter paper (type 2) or degreased cotton into the bottom stem of the separating funnel. Remove the water by passing the organic phase through this, or transfer the organic phase to a stoppered Erlenmeyer flask, containing sodium sulfate (anhydrous), and shake to dehydrate.

2) For the standard solutions used in generating the calibration curve, accurately transfer increasing volumes of Cu standard solution (5µg of Cu/m*l*) from 0 – 4.0m*l* (containing 0 – 20µg of Cu) into several beakers. The remainder of the procedure is the same as described in 1). The resulting solution is used for measurement.

Measurement:

Measurement wavelength : 324.8nm

Calibration curve range : 0.1 – 1µg/m*l*

Measurement Conditions :

Slit width : 0.5nm
Lamp mode : BGC-$D_2$
Burner height : 7mm
Support gas : Air
Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- Fe

Reagents:

1) Fe standard solution (5µg of Fe/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Tartaric acid solution (40 w/v%)
3) Diethyl ammonium diethyldithiocarbamate (DADDC) solution
4) Ammonium pyrrolizidine dithiocarbamate (APDC) solution
5) n-butyl acetic acid
6) Methyl red solution

2) – 6) are prepared as described for Cu, Reagents, 2) – 6)

Procedure:

1) Take an aliquot from the sample solution containing 10 – 40µg of Fe, and transfer to a 200m*l* beaker. The remainder of the procedure is as described for Cu, Procedure, 1).
2) For the standard solutions used in generating the calibration curve, accurately transfer increasing volumes of Fe standard solution (10µg of Fe/m*l*) from 0 – 4.0m*l* (containing 0 – 40µg of Fe) into several beakers. The remainder of the procedure is the same as described in 1). The resulting solution is used for measurement.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.2 – 2µg/m*l*

Measurement Conditions :

Lamp current : 12 mA
Slit width : 0.2nm
Lamp mode : BGC-$D_2$
Burner height : 7mm
Support gas : Air

Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- Mn

Reagents:

1) Mn standard solution (20μg of Mn/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Magnesium chloride solution: Dissolve 105g of magnesium chloride in water, and dilute to 250m*l*.(20m*l* of this solution contains 1.0g of Mg).

Procedure:

1) The pretreated sample solution is measured just as it is.

   For blank measurement, take an appropriate amount of reagent containing no sample, and perform the same pretreatment as that used for the sample. Then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.
2) For the standard solutions used in generating the calibration curve, add 20m*l* of the magnesium chloride solution to each of several 100m*l* volumetric flask. Accurately add increasing volumes of Mn standard solution (20μg of Mn/m*l*) from 0 – 10m*l* (containing 0 – 200μg of Mn) into several beakers. Bring up to volume with water and use this solution for measurement.

Measurement:

Measurement wavelength : 279.5nm
Calibration curve range : 0.2 – 2μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 22)

- Ni

Reagents:

1) Ni standard solution (5μg of Ni/m*l*): Refer to Cookbook Section 2, Item 3 Preparing Standards
2) Tartaric acid solution (40 w/v%)
3) Diethyl ammonium diethyldithiocarbamate (DADDC) solution
4) Ammonium pyrrolizidine dithiocarbamate (APDC) solution
5) n-butyl acetic acid
6) Methyl red solution

   2) – 6) are prepared as described for Cu, Reagents, 2) – 6)

Procedure:

1) Take an aliquot from the sample solution containing 5 – 20μg of Ni, and transfer to a

200m*l* beaker. The remainder of the procedure is as described for Cu, Procedure, 1).

2) For the standard solutions used in generating the calibration curve, accurately transfer increasing volumes of Ni standard solution (5µg of Ni/m*l*) from 0 – 4.0m*l* (containing 0 – 20µg of Ni) into several beakers. The remainder of the procedure is the same as described in 1). The resulting solution is used for measurement.

Measurement:

Measurement wavelength : 232.0nm
Calibration curve range : 0.2 – 1.0µg/m*l*
Measurement Conditions :
Lamp current : 12 mA
Slit width : 0.2nm
Lamp mode : BGC-$D_2$
Burner height : 7mm
Support gas : Air
Fuel gas flow rate : $C_2H_2$ 0.8*l*/min (If flame appears reddish when sample is sprayed, decrease the amount of sample suctioned.)

- Zn

Reagents:

1) Zn standard solution (5µg of Zn/m*l*)
2) Zn standard solution (2µg of Zn/m*l*)
   For 1) and 2), refer to Cookbook Section 2, Item 3 Preparing Standards
3) Magnesium chloride solution: Same as described for Mn, Reagents, 2)

Procedure:

1) If the percent of Zn contained in the pretreated sample solution is less than 0.001 %, that solution is measured as it is. If the sample solution contains more than 0.001 % Zn, use an aliquot specified in the following table, and bring up to volume with water.

| Percent Zn contained (%) | Aliquot (m*l*) | Volumetric flask (m*l*) |
|---|---|---|
| 0.001– 0.02 | 20 | 100 |
| 0.02 – 0.05 | 10 | 100 |

For blank measurement, perform the same procedure on the reagent containing no sample as that performed for pretreatment of the sample. Then measure this solution. The obtained value may be used for the correction of the value obtained in sample measurement.

2) For the standard solutions used to generate the calibration curve, if the amount of Zn in the sample solution is less than 0.001 %, transfer 20m*l* of magnesium chloride solution to each of several 100m*l* volumetric flasks. Accurately add increasing volumes of Zn standard solution (2µg of Zn/m*l*) from 0 – 5.0m*l* (containing 0 – 10µg of Zn), and bring up to volume with water.

If the amount of Zn is less than 0.001 %, transfer 4m*l* of hydrochloric acid (1+1) to each of several 100m*l* volumetric flasks. Accurately add increasing volumes of Zn standard solution (5µg of Zn/m*l*) from 0 – 10.0m*l* (containing 0 – 50µg of Zn), and bring up to volume with water.

Measurement:

Measurement wavelength : 213.9nm
Calibration curve range : 0.02 – 0.5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 44)

## 15.15 Solder Analysis Method

Reference Materials: Japan Industrial Standard, Solder Analysis Method JIS Z 3910

The solder referred to here corresponds to the following items specified in the Japan Industrial Standard JIS Z 3910:

Pb97.5Ag, Pb97.5SnAg1.5
Pb98Sn, Pb95Sn, Pb90Sn, Pb80Sn, Pb70Sn, Pb65Sn
Pb60Sn, Pb55Sn
Sn50Pb, Sn55Pb, Sn60Pb, Sn63Pb, Sn65Pb
Sn62PbAg2
Sn43PbBi14
Bi58Sn

### 15.15.1 Sample Pretreatment

a) Al

Weigh out 30g of sample and transfer to a 300m*l* beaker. Add 30m*l* of hydrobromic acid-bromine mixture and heat to decompose. To this add 20m*l* of sulfuric acid and heat until the white fumes of sulfuric acid are generated. Then, little by little add 10m*l* of hydrobromic acid. Heat to volatilize the tin, antimony, arsenic, etc. until the volume is concentrated to about 10m*l*. After cooling, add 50m*l* of water, and heat to dissolve the soluble salts.

After cooling, filter out the lead sulfate precipitate using Type 5C filter paper, and rinse with sulfuric acid (2+100). Transfer the filtrate and rinse liquid to a separate tall 300m*l* beaker using water, and heat until evaporated. Add 10m*l* of hydrochloric acid and 10m*l* of nitric acid to this dry beaker, and heat to dissolve all the soluble salts, concentrating the liquid to a volume of about 20m*l*. After cooling to ambient temperature, transfer to 50m*l* volumetric flask using water, and bring up to volume with water.

Note: Hydrobromic acid-bromine mixture: Add 20m*l* of bromine to 180m*l* of hydrogen bromide, and mix by shaking.

b) Bi, Cd, Cu, Fe, Pb, Sb, Zn

Weigh out 1.0g of sample. Transfer to a 300m*l* beaker, cover with a watch glass, add 50m*l* of acid mixture, and after heating to decompose, continue heating until total volume decreases to 10 – 20m*l*. After cooling to ambient temperature, transfer to a 100m*l* volumetric flask and bring up to volume with water. Let stand for about one hour, and then filter using Type 5C filter paper.

Note: Acid mixture: 85 parts hydrochloric acid, 10 parts nitric acid, 5 parts water

15.15.2 Flame Atomic Absorption Method

a) Target elements and quantitation range

| Element | Percent contained (%) |
|---|---|
| Al | <0.01 |
| Bi | <0.05 |
| Cd | <0.005 |
| Cu | <0.05 |
| Fe | <0.05 |
| Pb | <0.1 |
| Sb | <0.5 |
| Zn | <0.005 |

b) Measurement procedure

Measurement is conducted using the following procedure. Refer to Cookbook Section 3, Item 6.4 Element Specific Measurement Conditions, for the lamp current, slit width and flame conditions.

- Al

Reagents:

Al standard solution (50μg of Al/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step a) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Al standard solution is prepared and measured, and the value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, weigh out several 3.0g lots containing the elements contained in the sample at about the same ratio as that in the sample. Transfer these to several tall 300m*l* beakers, respectively. Add increasing volumes of the Al standard solution (50µg of Al/m*l*) from 0 – 10.0m*l* (Al content from 0 – 500µg). The remainder of the procedure is the same as that used in the sample pretreatment step a) for Al. Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 309.3nm
Calibration curve range : 2 – 10µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 2)

- Bi (Not applicable for Sn43PbBi14)

Reagents:

Bi standard solution (100µg of Bi/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Bi standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample. Transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Bi standard solution (100µg of Bi/m*l*) from 0 – 10.0m*l* (Bi content from 0 – 1000µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 223.1nm
Calibration curve range : 1 – 10µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 8)

- Cd

Reagents:

Cd standard solution (20µg of Cd/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank

measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cd standard solution. The value obtained can be used to correct the value obtained in sample measurement.

2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Cd standard solution (20µg of Cd/m*l*) from 0 – 5.0m*l* (Cd content from 0 – 100µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 228.8nm
Calibration curve range : 0.05 – 1µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 11)

- Cu

Reagents:

Cu standard solution (50µg of Cu/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Cu standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Cu standard solution (50µg of Cu/m*l*) from 0 – 10.0m*l* (Cu content from 0 – 500µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 324.8nm
Calibration curve range : 0.2 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 15)

- Fe

Reagents:

Fe standard solution (50µg of Fe/m*l*): refer to Cookbook Section 2, Item 3 Preparing

Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Fe standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Fe standard solution (50µg of Fe/m*l*) from 0 – 10.0m*l* (Fe content from 0 – 500µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 248.3nm
Calibration curve range : 0.2 – 5µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 16)

- Pb (Applicable for Bi58Sn, Sn96.5Ag and Sn95Sb)

Reagents:

Pb standard solution (100µg of Pb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

Procedure:

1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Pb standard solution. The value obtained can be used to correct the value obtained in sample measurement.
2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Pb standard solution (100µg of Pb/m*l*) from 0 – 20.0m*l* (Pb content from 0 – 2000µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 283.3nm
Calibration curve range : 2 – 20µg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 27)

- Sb (Not applicable for Sn95Sb)

  Reagents:

  Sb standard solution (500µg of Sb/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

  Procedure:

  1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Sb standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Sb standard solution (500µg of Sb/m*l*) from 0 – 10.0m*l* (Sb content from 0 – 5000µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

  Measurement:

  Measurement wavelength : 217.6nm
  Calibration curve range : 2 – 50µg/m*l*
  Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 32)

- Zn

  Reagents:

  Zn standard solution (20µg of Zn/m*l*): refer to Cookbook Section 2, Item 3 Preparing Standards

  Procedure:

  1) The sample solution pretreated according to step b) is measured just as it is. For blank measurement, when preparing the standards for generating the calibration curve, prepare and measure a solution containing no added Zn standard solution. The value obtained can be used to correct the value obtained in sample measurement.
  2) For the standard solutions to be used in generating the calibration curve, weigh out several 1.0g lots containing the elements contained in the sample at about the same ratio as that in the sample, and transfer these to several 300m*l* beakers, respectively. Add increasing volumes of the Zn standard solution (20µg of Sb/m*l*) from 0 – 5.0m*l* (Zn content from 0 – 100µg). The remainder of the procedure is the same as that used in the sample pretreatment step b). Use the resulting solution for measurement.

Measurement:

Measurement wavelength : 213.9nm
Calibration curve range : 0.5 – 1μg/m*l*
Measurement conditions : Refer to Cookbook Section 3, Item 6.4, 44)

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# Atomic Absorption Analysis Cookbook

## Section 9

### Non-ferrous Metals Analysis (II)

### Iron and Steel Analysis

SHIMADZU CORPORATION
KYOTO, JAPAN

## Table of Contents

## Introduction

Cookbook Section 9 describes analysis methods for non-ferrous metals, iron and steel.

The analysis methods described here are accepted by the Japan Industrial Standard as methods of elemental analysis using the atomic absorption analysis method. The techniques of these described analysis methods were modified for analysis using the Shimadzu Atomic Absorption Spectrophotometer.

These methods assume the analysis of samples having a fixed composition according to the Japan Industrial Standard, however, the composition of samples in actual analysis may differ from those specified in the Japan Industrial standard. In these cases, the pretreatment procedure, interference, background absorption and flame conditions, etc. may not always be optimum.

In addition, since these measurement conditions are set with respect to the Shimadzu AA-6000 Series Atomic Absorption Spectrophotometer, it is necessary to modify such pretreatment conditions as sample amount, etc., as well as the measurement conditions and calibration curve concentration range when another type of atomic absorption spectrophotometer is used.

NOTE: Filter Paper

There are several references to the use of filter paper in the procedures described in this documentation. All of these are referred to using the designation of Advantec Mfs. Inc. These correspond to other manufacturers' products, as follows.

| Advantec | Whatman | Schleicher & Schuell |
|---|---|---|
| 5A | 41 | 589 Black |
| 5B | 40 | 589 White |
| 5C | 42 | 589 Red |
| 6 | 44 | 589 Blue |

# 16. Non-ferrous Metals Analysis

## 16.1 Titanium and Titanium Alloy Analysis Method

Reference Materials

Japan Industrial Standard

| | |
|---|---|
| Quantitation Method for Manganese in Titanium and Titanium Alloy | JIS H 1613 |
| Quantitation Method for Iron in Titanium and Titanium Alloy | JIS H 1614 |
| Quantitation Method for Magnesium in Titanium and Titanium Alloy | JIS H 1616 |
| Quantitation Method for Sodium in Titanium and Titanium Alloy | JIS H 1623 |

### 16.1.1 Sample Pretreatment

a) Fe, Mg, Mn

Weigh out 0.50g of sample (for Mn, 1.0g) to the nearest 1mg, and transfer to a 200mL polyethylene beaker. Add 10mL of hydrochloric acid (1+1) and 5mL of hydrofluoric acid (1+1), cover with a polyethylene watch glass, and heat gently over a water bath to decompose. Drip 3mL of nitric acid (1+1) into the beaker, and after heating again to volatilize the nitrogen oxide, wash the bottom of the watch glass with water, and remove the watch glass. Add 3g of boric acid, mix thoroughly to dissolve, and cool to ambient temperature. Transfer the solution to a 100mL volumetric flask, and bring to volume with water.

b) Na

Weigh out 1.0g of sample to the nearest 1mg, and transfer to a 300mL polyethylene beaker. Add 40mL of water and, little by little, 10mL of hydrofluoric acid (1+1). Cover with a polyethylene watch glass, and heat gently over a water bath to decompose. Drip 3mL of nitric acid (1+1) into the beaker, and heating again to volatilize the nitrogen oxide. Wash the bottom of the watch glass with water, and remove the watch glass. Add 3g of boric acid, mix thoroughly to dissolve, and cool to room temperature. Transfer the solution to a 500mL volumetric flask, bring to volume with water, and transfer the contents to a dry polyethylene bottle.

16.1.2 Flame Atomic Absorption Method

a) Target Elements and Quantitation Range

| Element | Content (%) |
|---|---|
| Fe | ≥0.005, ≤2.0 |
| Mg | ≥0.01, ≤1.0 |
| Mn | ≥0.001 |
| Na | ≥0.01, ≤0.2 |

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current, slit width and flame conditions, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

I Fe

Reagents

(1) Fe standard solution (50µg Fe/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ti : Greater than 99% pure with as little Fe as possible, known percentages

Procedure

(1) If the sample contains less than 0.1% of Fe, the solution prepared in a) Fe, Mg, Mn may be used as is for measurement. If the sample contains between 0.1% and 0.5% of Fe, transfer a 20mL aliquot of the sample solution to a 100mL volumetric flask, add 8mL of hydrochloric acid (1+1), bring to volume with water, and use this solution for measurement. If the sample contains between 0.5% and 2.0% of Fe, transfer a 5mL aliquot of the sample solution to a 100mL volumetric flask, add 9.5mL of hydrochloric acid (1+1), bring to volume with water, and use this solution for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Fe standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, when the Fe content is less than 0.1%, prepare several polyethylene beakers (200mL), and weigh into each of these 0.50g of Ti. After performing the same procedure as that described in Sample Pretreatment, a) Fe, Mg, Mn, accurately add Fe standard solution (50µg Fe/mL) in incrementally increasing volumes from 0 - 10.0mL (0 - 0.5mg of Fe) to these beakers, and dilute to 200mL using water.

If the Fe content is between 0.5% and 2.0%, prepare several polyethylene beakers (200mL), and weigh into each of these 0.50g of Ti. After performing the same procedure as that described in Sample Pretreatment, a) Fe, Mg, Mn, use an aliquot as described in procedure step (1), and accurately add Fe standard solution (50µg Fe/mL) in incrementally increasing volumes from 0 - 10.0mL (0 - 0.5mg of Fe) to these beakers, and dilute to 200mL using water.

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |
| Calibration curve concentration range | 0.5 - 5µg/mL |
| Measurement conditions | Refer to Cookbook Section 2, Paragraph 6.4, 16) |

### I Mg

Reagents

(1) Mg standard solution (10µg Mg/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ti : Greater than 99% pure with as little Mg as possible, known percentages

(3) Strontium chloride solution : Dissolve 10g of strontium chloride-6H2O in water, and bring the final volume to 100mL using water

Procedure

(1) Transfer to a 100mL volumetric flask a 10mL aliquot of the solution prepared according to Sample Pretreatment a) Fe, Mg, Mn. Add 5mL of hydrochloric acid (1+1) and 5mL of strontium chloride solution, and bring to volume with water.

For the blank test, using the same amount of reagent as that of the pretreated sample, perform the same pretreatment procedure as that for the sample, and use this solution for measurement. The result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, weigh out 1.0g of Ti and transfer it to a polyethylene beaker (200mL). After performing the same procedure as that described in Sample Pretreatment, a) Fe, Mg, Mn, transfer several 10mL aliquots of this solution to each of several 100mL volumetric flasks. Accurately add Mg standard solution (10µg Mg/mL) in incrementally increasing volumes from 0 - 10.0mL (0 - 0.1mg of Mg) to each of these flasks, add 5mL of hydrochloric acid (1+1) and 5mL of strontium chloride solution, and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 285.2nm |
| Calibration curve concentration range | 0.05 - 1µg/mL |
| Measurement conditions | Refer to Cookbook Section 2, Paragraph 6.4, 21) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### I Mn

Reagents

(1) Mn standard solution (10µg Mn/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing

Standards

(2) Ti : Greater than 99% pure with as little Mn as possible, known percentages

Procedure

(1) The solution prepared according to Sample Pretreatment a) Fe, Mg, Mn is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Mn standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several polyethylene beakers (200mL). Weigh into each of these 1.0g of Ti, and after performing the same procedure as that described in Sample Pretreatment, a) Fe, Mg, Mn, accurately add Mn standard solution (10µg Mn/mL) in incrementally increasing volumes from 0 - 5.0mL (0 - 0.05mg of Mn) to these beakers, and dilute to 200mL with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 279.5nm |
| Calibration curve concentration range | 0.05 - 0.5µg/mL |
| Measurement conditions | Refer to Cookbook Section 2, Paragraph 6.4, 22) |

I Na

Reagents

(1) Na standard solution (100µg Fe/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ti : Greater than 99% pure with as little Na as possible, known percentages

Procedure

(1) The solution prepared according to Sample Pretreatment b) Na is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Na standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several polyethylene beakers (300mL). Weigh into each of these 1.0g of Ti, and after performing the same procedure as that described in Sample Pretreatment, b) Na, accurately add Na standard solution (100µg Na/mL) in incrementally increasing volumes from 0 - 20.0mL (0 - 2mg of Mn) to these beakers, and dilute to 300mL with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 589.0nm |
| Calibration curve concentration range | 0.1 - 4µg/mL |
| Measurement conditions | Refer to Cookbook Section 2, Paragraph 6.4, 24) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

## 16.2 Gallium Arsenide Crystals Analysis

Reference Materials

Japan Industrial Standard

Gallium Arsenide Crystals Analysis Method JIS H 1191

### 16.2.1 Sample Pretreatment

a) Cr, Cu, Fe, In, Mn, Zn

I Sample weights

Referring to the following table, weigh out the sample according to the percent content of the target element.

| Element | Content (%) | Weight (g) |
|---|---|---|
| Cr | 0.00002 - 0.0010 | 0.10 |
| Cu | 0.00005 - 0.0010 | 0.10 |
| Fe | 0.00005 - 0.0010 | 0.10 |
| In | 0.0010 - 0.020 | 0.50 |
|  | 0.020 - 0.20 | 0.20 |
|  | 0.20 - 0.80 | 0.10 |
| Mn | 0.00001 - 0.0010 | 0.10 |
| Zn | 0.0002 - 0.050 | 0.50 |

I Preparing Sample Solution

Weight out the sample and transfer it to a test tube (with 10mL and 20mL indications). Add approximately 3mL of hydrochloric acid (1+1) and gently shake to mix, and after discarding only the solution, wash several times each with approximately 5mL of high purity water. Add 5mL of hydrochloric acid (1+1) and 2.5mL of nitric acid, and after heating at 50 - 70°C to decompose, continue heating until the liquid is concentrated to about 5mL. After cooling to ambient temperature, fill with high purity water to the 20mL indication (When weight of In, Zn sample is 0.5g, fill to 10mL indication).

Notes:

(1) Hydrochloric acid (1+1) : Mix 1 part hydrochloric acid and 1 part water, and purify by non-boiling distillation using a quartz distiller. Store the acid in a PTFE container.

(2) Nitric acid : Purify by non-boiling distillation using a quartz distiller. Store the acid in a PTFE container.

b) Te

Weigh out the sample (for Te content 0.0001 - 0.0005% use 0.40g, for 0.0005 - 0.002% use 0.10g) and transfer it to a 100mL beaker. Add approximately 3mL of hydrochloric acid (1+1) and gently shake to mix, and after discarding only the solution, wash several times each with approximately 5mL of high purity water. Cover with a watch glass, and add 10mL of hydrochloric acid (1+1) and 5mL of nitric acid, and after heating at 50 - 70°C to decompose, continue heating until the sample is dry. After cooling, wash the bottom of the watch glass with water and remove the watch glass, and heat until dry again.

Add 3mL of hydrochloric acid and heat to dissolve, and after cooling, add 0.5mL of Ni solution (5mg Ni/mL). Using 12mL more of hydrochloric acid, transfer to a 100mL separatory funnel, and bring volume to 25mL using high purity water. Add 25mL of isopropyl ether, and shake for about 10 minutes to mix. Set aside for about 30 minutes to allow formation of 2 separate layers, and transfer the aqueous phase to a dry 50mL beaker. This solution is used for measurement.

Notes:

(1) Hydrochloric acid (1+1) and Nitric acid : Same as those described in Notes (1) and (2) for Preparing Sample Solution under a) Cr, Cu, Fe, In, Mn, Zn

(2) Ni solution (5mg Ni/mL) : Add 30mL of nitric acid (1+1) to 0.100g of Ni (≥99.9 wt%), and after cooling, dilute to 200mL with water.

### 16.2.2 Furnace Atomic Absorption Method

a) Target Elements and Quantitation Range

| Element | Content (%) |
|---|---|
| Cr | 0.00002 - 0.0010 |
| Cu | 0.00005 - 0.0010 |
| Fe | 0.00005 - 0.0010 |
| Mn | 0.00001 - 0.0010 |
| Te | 0.0001 - 0.0020 |

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current and slit width, refer to Cookbook Section 4, Paragraph 7.5 Measurement Conditions According to Element.

I Cr

Reagents

(1) Cr standard solution (500ng Cr/mL)

(2) Cr standard solution (100ng Cr/mL)

For preparation of (1) and (2), refer to Cookbook Section 2, Item 3 Preparing Standards

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) If the percent content of Cr in the sample is 0.00002 - 0.0003%, the sample solution prepared according to Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn is measured as is. If the percent content of Cr is 0.0003 - 0.0010%, an aliquot taken from the sample solution after diluting it by a factor of 5 times is used for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Cr standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several 0.05g portions of Ga (99.9999 wt%) and 0.05g portions of As (99.9999 wt%), and transfer each of these to a test tube. Prepare a solution according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool it to ambient temperature. If the percent content of Cr in the sample is 0.00002 - 0.0003%, accurately add Cr standard solution (2) (100ng Cr/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 300ng of Cr) to the test tubes, and dilute these with high purity water to the 20mL indication. Use these as standard solutions.

If the percent content of Cr is 0.0003 - 0.0010%, accurately add Cr standard solution (1) (500ng Cr/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 1500ng of Cr) to the test tubes, and dilute these with high purity water to the 20mL indication. Then dilute these by a factor of 5 times, and use these as standard solutions.

Measurement

| | |
|---|---|
| Measurement wavelength | 357.9nm |
| Calibration curve concentration range | 1.0 - 15ng/mL |
| Tube | Pyrolytic graphite tube |
| Sample injection volume | 10µL |

Heating Conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 800 | 10 | R | 1.0 |
| 4 | 800 | 15 | S | 1.0 |
| 5 | 800 | 3 | S | 0.0 |
| 6 | 2500 | 3 | S | 0.0 |
| 7 | 2800 | 2 | S | 1.0 |

## I Cu

Reagents

(1) Cu standard solution (500ng Cu/mL)

(2) Cu standard solution (100ng Cu/mL)

For preparation of (1) and (2), refer to Cookbook Section 2, Item 3 Preparing Standards

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) If the percent content of Cu in the sample is 0.00005 - 0.0003%, the sample solution prepared according to Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn is measured as is. If the percent content of Cu is 0.0003 - 0.0010%, an aliquot taken from the sample solution after diluting it by a factor of 5 times is used for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Cu standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several 0.05g portions of Ga (99.9999 wt%) and 0.05g portions of As (99.9999 wt%), and transfer each of these to a test tube. Prepare a solution according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool it to ambient temperature. If the percent content of Cu in the sample is 0.00005 - 0.0003%, accurately add Cu standard solution (2) (100ng Cu/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 300ng of Cu) to the test tubes, and dilute these with high purity water to the 20mL indication. Use these as standard solutions.

If the percent content of Cu is 0.0003 - 0.0010%, accurately add Cu standard solution (1) (500ng Cu/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 1500ng of Cu to the test tubes, and dilute these with high purity water to the 20mL indication. Then dilute these by a factor of 5 times, and use these as standard solutions.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.8nm |
| Calibration curve concentration range | 1.0 - 15ng/mL |
| Tube | Pyrolytic graphite tube |
| Sample injection volume | 10µL |

Heating Conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 15 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0 |
| 6 | 2400 | 3 | S | 0.0 |
| 7 | 2700 | 2 | S | 1.0 |

**I** Fe

Reagents

(1) Fe standard solution (500ng Fe/mL)

(2) Fe standard solution (100ng Fe/mL)

For preparation of (1) and (2), refer to Cookbook Section 2, Item 3 Preparing Standards

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) If the percent content of Fe in the sample is 0.00005 - 0.0003%, the sample solution prepared according to Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn is measured as is. If the percent content of Cu is 0.0003 - 0.0010%, an aliquot taken from the sample solution after diluting it by a factor of 5 times is used for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Fe standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several 0.05g portions of Ga (99.9999 wt%) and 0.05g portions of As (99.9999 wt%), and transfer each of these to a test tube. Prepare a solution according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool it to ambient temperature. If the percent content of Fe in the sample is 0.00005 - 0.0003%, accurately add Fe standard solution (2) (100ng Fe/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 300ng of Fe) to the test tubes, and dilute these with high purity water to the 20mL indication. Use these as standard solutions.

If the percent content of Fe is 0.0003 - 0.0010%, accurately add Fe standard solution (1) (500ng Fe/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 1500ng of Fe to the test tubes, and dilute these with high purity water to the 20mL indication. Then dilute these by a factor of 5 times, and use these as standard solutions.

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |
| Calibration curve concentration range | 1.0 - 15ng/mL |
| Tube | Pyrolytic graphite tube |
| Sample injection volume | 20µL |

Heating Conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 15 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0 |
| 6 | 2400 | 3 | S | 0.0 |
| 7 | 2700 | 2 | S | 1.0 |

## **I** Mn

Reagents

(1) Mn standard solution (250ng Mn/mL)

(2) Cu standard solution (50ng Mn/mL)

For preparation of (1) and (2), refer to Cookbook Section 2, Item 3 Preparing Standards

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) If the percent content of Mn in the sample is 0.00001 - 0.0002%, the sample solution prepared according to Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn is measured as is. If the percent content of Mn is 0.0002 - 0.0010%, an aliquot taken from the sample solution after diluting it by a factor of 5 times is used for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Mn standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several 0.05g portions of Ga (99.9999 wt%) and 0.05g portions of As (99.9999 wt%), and transfer each of these to a test tube. Prepare a solution according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool it to ambient temperature. If the percent content of Mn in the sample is 0.00001 - 0.0002%, accurately add Mn standard solution (2) (50ng Mn/mL) in incrementally increasing volumes from 0 - 4.0mL (0 - 200ng of Mn) to the test tubes, and dilute these with high purity water to the 20mL indication. Use these as standard solutions.

If the percent content of Mn is 0.0002 - 0.0010%, accurately add Mn standard solution (1) (250ng Mn/mL) in incrementally increasing volumes from 0 - 4.0mL (0 - 1000ng of Mn to the test tubes, and dilute these with high purity water to the 20mL indication. Then dilute these by a factor of 5 times, and use these as standard solutions.

Measurement

| | |
|---|---|
| Measurement wavelength | 279.5nm |
| Calibration curve concentration range | 0.5 - 10ng/mL |
| Tube | Pyrolytic graphite tube |
| Sample injection volume | 10µL |
| Heating Conditions | |

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 15 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0 |
| 6 | 2400 | 3 | S | 0.0 |
| 7 | 2700 | 2 | S | 1.0 |

**I** Te

Reagents

(1) Te standard solution (400ng Te/mL) : Add 20mL of nitric acid (1+1) to 0.100g of Te (≥99.9 wt%) and heat to dissolve. After cooling to ambient temperature, transfer to a 1000mL volumetric flask using water, and bring up to volume to produce a source solution (100µg Te/mL). Transfer 10.0mL of this source solution to a 250mL volumetric flask, bring up to volume with water, and then accurately dilute this solution with water by a factor of 10 times.

(2) Ga : ≥99.9999 wt%

(3) As : ≥99.9999 wt%

Procedure

(1) The solution prepared according the to sample pretreatment procedure b) Te is used as is for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Te standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several portions of Ga (99.9999 wt%) and As (99.9999 wt%), each 1/2 the amount of weighed sample, and transfer each of these to a 100mL beaker. Cover each with a watch glass, add 10mL of hydrochloric acid (1+1) and 5mL of nitric acid, heat at 50 - 70°C to dissolve, and then cool. Accurately add Te standard solution (400ng Te/mL) in incrementally increasing volumes from 0 - 5.0mL (0 - 2000ng of Te) to the beakers, and heat until dry. Thereafter, follow the procedure described in Sample Pretreatment b) Te, from “Add 3mL of hydrochloric acid and...”, and use the resultant solution for measurement.

Measurement

|  |  |
|---|---|
| Measurement wavelength | 214.3nm |
| Lamp current | 14mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Calibration curve concentration range | 10 - 80ng/mL |
| Tube | High density graphite tube |
| Sample injection volume | 20µL |

Heating Conditions

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 100 | 20 | R | 0.2 |
| 2 | 250 | 10 | R | 0.2 |
| 3 | 500 | 10 | R | 1.0 |
| 4 | 500 | 15 | S | 1.0 |
| 5 | 500 | 3 | S | 0.0H |
| 6 | 2100 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

### 16.2.3 Flame Atomic Absorption Method

a) Target Elements and Quantitation Range

| Element | Content (%) |
|---|---|
| In | 0.001 - 0.80 |
| Zn | 0.0002 - 0.050 |

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current, slit width and flame conditions, refer to Cookbook Section 6, Paragraph 6.4 Measurement Conditions According to Element. For preparing standards used in generating a calibration curve, refer to Cookbook Section 2, Item 3 Preparing Standards.

**I** In

Reagents

(1) In standard solution (100µg In/mL) : Add 20mL of hydrochloric acid (1+1) to 0.100g of In (≥99.0wt%), and heat to dissolve. After cooling to ambient temperature, transfer to 1000mL volumetric flask using water, and bring to volume with water.

(2) In standard solution (40µg In/mL) : Transfer 100mL of In standard solution (1) (100µg In/mL) to a 250mL volumetric flask, and bring to volume with water. (Prepare at each new usage)

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) Solutions prepared according to Sample Pretreatment a) Cr, Cu, Fe, In, Mn, Zn are used as is.

For the blank test, the solution used for diluting standards is measured as is without adding any In standard solution, and the result is used to correct subsequent standard and sample measurement values.

To prepare the standard solutions for the calibration curve, weigh out several portions of Ga (99.9999 wt%) and As (99.9999 wt%), each at one half the amount of sample used, and transfer each of these to a test tube. Prepare sample solutions according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool each to ambient temperature. When the amount of sample is 0.50g, accurately add In standard solution (2) (40µg In/mL) in incrementally increasing volumes from 0 - 3.0mL (0 - 120µg of In) to the test tubes, and dilute these with high purity water to the 10mL indication.

When the amount of sample is 0.20g, accurately add In standard solution (2) (40µg In/mL) in incrementally increasing volumes from 0 - 10.0mL (0 - 400µg of In) to the test tubes, and dilute these with high purity water to the 20mL indication.

When the amount of sample is 0.10g, accurately add In standard solution (1) (100µg In/mL) in incrementally increasing volumes from 0 - 8.0mL (0 - 800µg of In) to the test tubes, and dilute these with high purity water to the 20mL indication.

Measurement

| | |
|---|---|
| Measurement wavelength | 303.9nm |
| Calibration curve concentration range | 1 - 40µg/ml |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | C2H2  2.0 L/min |

### I Zn

Reagents

(1) Zn standard solution (50µg Zn/mL)

(2) Zn standard solution (5µg Zn/mL)

For reagents (1) and (2), refer to Cookbook Section 2, Item 3  Preparing Standards

(3) Ga : ≥99.9999 wt%

(4) As : ≥99.9999 wt%

Procedure

(1) If the percent content of Zn in the sample is 0.0002 - 0.004%, the sample solution prepared according to Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn is measured as is. If the percent content of Zn is 0.004 - 0.050%, an aliquot taken from the sample solution after diluting it by a factor of 10 times is used for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Zn standard solution, and the

result is used to correct subsequent standard and sample measurement values.

(2) To prepare the standard solutions for the calibration curve, weigh out several 0.25g portions of Ga (99.9999 wt%) and 0.25g portions of As (99.9999 wt%), and transfer each of these to a test tube. Prepare a solution according to the procedure described in Sample Pretreatment for a) Cr, Cu, Fe, In, Mn, Zn, and cool it to ambient temperature. If the percent content of Zn in the sample is 0.0002 - 0.004%, accurately add Zn standard solution (2) (5µg Zn/mL) in incrementally increasing volumes from 0 - 4.0mL (0 - 20µg of Zn) to the test tubes, and dilute these with high purity water to the 10mL indication.

If the percent content of Zn in the sample is 0.004 - 0.050%, accurately add Zn standard solution (1) (50µg Zn/mL) in incrementally increasing volumes from 0 - 5.0mL (0 - 250µg of Zn) to the test tubes, and dilute these with high purity water to the 10mL indication. Then dilute these by a factor of 10 times, and use these as standard solutions.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Calibration curve concentration range | 0.1 - 2.5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, Item 44 |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

## 17. Iron and Steel Analysis

Iron and Steel Analysis Method

Reference Materials

Japan Industrial Standard

Atomic Absorption Analysis Method for Iron and Steel JIS G 1257

### 17.1.1 Sample Pretreatment

a) Direct Acid Decomposition Method

I Al I (Samples easily decomposed using mixed acid)

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of mixed acid (1 part hydrochloric acid, 1 part nitric acid, 2 parts water), heat to decompose, and continue heating until all of the nitrogen oxide, etc. is volatilized. Wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5C), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Save the filtrate and wash liquid as the main sample liquid.

As for the remaining undissolved material, transfer it along with the filter paper to a platinum crucible (No. 30), and after drying, heat strongly until the paper turns to ash, and then cool to ambient temperature. Moisten the remaining material with 2 or 3 drops of sulfuric acid, add 5mL of hydrofluoric acid, and heat gently until the silicon dioxide and sulfuric acid are volatilized. Add 1g of sodium disulfate, cover and heat gradually at first, raising the temperature gradually to a dark red heat until the remaining material becomes molten. After cooling to ambient temperature, add 10mL of hydrochloric acid (1+3) to the platinum crucible, heat gently to dissolve all the soluble material, and combine with the stored main sample liquid. Wash the platinum crucible with a small amount of water, and combine wash liquid with the main sample liquid. Using water, transfer the solution to a 100mL volumetric flask, and after cooling to ambient temperature, bring up to volume with water.

### Al II (Samples difficult to decompose using mixed acid)

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 300mL quartz beaker. Cover with a watch glass, add 15mL of aqua regia, and heat to decompose. Add 15mL of perchloric acid, and heat continuously until the white perchloric acid fumes are generated, and then continue heating until the perchloric acid fumes form condensate on the inside surface of the beaker for approximately 10 minutes. After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. The remainder of the procedure is the same as that described for Al I.

### Ca

Weigh out 2.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of aqua regia, and heat gently to decompose. Add 20mL of perchloric acid, and heat continuously until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 30mL of warm water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. Using type 5A filter paper, filter the solution into a 200mL beaker, wash alternately 5 or 6 times with warm perchloric acid (2+100) and warm water, finally washing adequately with warm water. Combine the filtrate with the wash liquid, and accurately add 10mL of La solution (50mg La/mL). Use this as the main sample solution.

As for the remaining undissolved material, transfer it along with the filter paper to a platinum crucible (No. 30), and after drying, heat strongly until the paper turns to ash, and then cool to ambient temperature. Moisten the remaining material with 2mL of perchloric acid, add 5mL of hydrofluoric acid, and heat gently until the silicon dioxide and perchloric acid are volatilized. Accurately weigh out and add 0.500g of sodium carbonate (anhydrous), cover and heat gradually at first, raising the temperature gradually to a dark red heat until the remaining material becomes molten. After cooling to ambient temperature, accurately add 10mL of hydrochloric acid to the platinum crucible, heat gently to dissolve all the soluble material, and combine with the main sample liquid. Wash the platinum crucible with a small amount of water, and combine wash liquid with the main sample liquid. Using water, transfer the solution to a 100mL volumetric flask, and after cooling to ambient temperature, bring up to volume with water.

**Note:** La solution (50mg La/mL) : Weigh out 58.6g of lanthanum oxide and transfer to a 500mL beaker. After adding approximately 200mL of water, little by little add 200mL of hydrochloric acid (1+1) while shaking to mix. Heat to dissolve the lanthanum oxide, then cool to ambient temperature, and finally add water to bring the volume to 1 liter.

### Co I (Samples easily decomposed using hydrochloric acid)

Weigh out 1.0g of sample (containing 0.01% - 0.10% of Co) or 0.20g of sample (containing 0.10% - 0.50% of Co) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of hydrochloric acid (1+1), and heat gently to decompose. Next, little by little add 5mL of hydrogen peroxide, heat to oxidize the iron, etc., and continue to boil until the excess hydrogen peroxide is decomposed. After cooling, wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

### Co II (Samples difficult to decompose using hydrochloric acid)

Weigh out the sample in the same way as for Co I, and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and heat continuously until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. The remainder of the procedure is the same as that described for Co I.

### Cr I (Samples easily decomposed using aqua regia)

Weigh out 1.0g of sample (containing 0.002% - 0.10% of Cr) or 0.20g of sample (containing 0.10% - 2.0% of Co) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, heat to decompose, and continue heating until the nitrogen oxide, etc. are volatilized. After cooling, add approximately 30mL of water, wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

### Cr II (Samples difficult to decompose using aqua regia)

Weigh out the sample in the same way as for Co I, and perform the same procedure as that for Cr I through the step of washing the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Save the filtrate and wash liquid as the main sample liquid.

As for the remaining undissolved material, transfer it along with the filter paper to a platinum crucible (No. 30), and after drying, heat strongly until the paper turns to ash, and then cool to ambient temperature. Moisten the remaining material with 2 or 3 drops of sulfuric acid (1+1), add 5mL of hydrofluoric acid, and heat gently until the silicon dioxide and sulfuric acid are volatilized. Add 1g of potassium disulfide, cover and heat gradually at first, raising the temperature gradually to a dark red heat until the remaining material becomes molten. After cooling to ambient temperature, add 5mL of hydrochloric acid (1+1) and a small amount of water to the platinum crucible, heat gently to dissolve all the remaining material, and combine wash liquid with the main sample liquid. Wash the platinum crucible and the cover with a small amount of water, and combine wash liquid with the main sample liquid. Using water, transfer the solution to a 100mL volumetric flask, and after cooling to ambient temperature, bring up to volume with water.

- Cu I (Samples easily decomposed using mixed acid)

Weigh out 1.0g of sample (containing 0.003% - 0.10% of Cu) or 0.50g of sample (containing 0.10% - 1.0% of Cu) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of mixed acid (1 part hydrochloric acid, 1 part nitric acid, 2 parts water), heat to decompose, and continue heating until the nitrogen oxide, etc. are volatilized. After cooling, wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

- Cu II (Samples difficult to decompose using mixed acid)

Weigh out the sample in the same way as for Cu I, and transfer to a 200mL beaker. The rest of the procedure is the same as that described for Co II.

- Mg

Weigh out 0.5g of sample (containing 0.001% - 0.040% of Mg) or 0.20g of sample (containing 0.040% - 1.0% of Mg) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. Using type 5A filter paper, filter the solution into a beaker, wash with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper, and combine the filtrate and wash liquid, discarding the remainder. Using water, transfer the solution to a 250mL volumetric flask, cool to ambient temperature, accurately add 4mL of La solution (50mg La/mL), and bring to volume with water.

Note: La solution (50mg La/mL) : Same as that described in Note for Ca

- Mn

Weigh out 1.0g of sample (containing 0.003% - 0.010% of Mn) or 0.50g of sample (containing 0.010% - 0.10% of Mn) or 0.20g of sample (containing 0.10% - 2.0% of Mn) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling to ambient temperature, add 10mL of hydrochloric acid (1+1) to dissolve the salts. Wash the bottom of the watch glass with water, and remove the watch glass. Using type 5A filter paper, filter the solution into a beaker, wash with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper, and combine the filtrate and wash liquid, discarding the remainder. Using water, transfer the solution to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

- Mo I (Samples easily decomposed using mixed acid A)

Weigh out 1.0g of sample (containing 0.01% - 0.50% of Mo) or 0.50g of sample (containing 0.50% - 1.0% of Mo) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of mixed acid A (1 part hydrochloric acid, 1 part nitric acid, 2 parts water), heat to decompose, and continue heating until the nitrogen oxide, etc. are volatilized.

Add 20mL of hydrochloric acid (1+1) to dissolve the salts. After cooling, wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, accurately add 10 mL of Al solution, cool to ambient temperature, and bring to volume with water.
Note: Al solution (12mg Al/mL) : Dissolve 110g of aluminum chloride •6H20 in water, and bring volume to 1 liter using water.

### Mo II (Samples difficult to decompose using mixed acid A)

Weigh out the sample in the same way as for Mo I, and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. The rest of the procedure is the same as that described for Mo I.

### Mo III (Samples containing tungsten)

Weigh out the sample in the same way as for Mo I, and transfer to a 200mL beaker. Cover with a watch glass, add 30mL of mixed acid B (1 part sulfuric acid, 1 part phosphoric acid, 16 parts water), heat to decompose, add 3mL of nitric acid, and heat to oxidize the iron, etc. Continue heating until the thick white fumes of sulfuric acid are generated. After cooling, add approximately 30mL of water and heat until the salts are dissolved. After cooling, wash the bottom of the watch glass with water, and remove the watch glass. The rest of the procedure is the same as that described for Mo 1.

### Ni I (Samples easily decomposed with mixed acid)

Same procedure as that for Cu I.

### Ni II (Samples difficult to decompose using mixed acid)

Weigh out 1.0g of sample (containing 0.003% - 0.10% of Ni) or 0.50g of sample (containing 0.10% - 1.0% of Ni) to the nearest 0.001g and transfer to a 200mL beaker. The rest of the procedure is the same as that described for Co II.

### Pb

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and heat continuously until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 20mL of warm water to dissolve the salts, wash the bottom of the watch glass with water, and remove the watch glass. Using type 5A filter paper, filter the solution into a 200mL beaker, wash 5 or 6 times with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

### Ti I (Samples easily decomposed with hydrochloric acid)

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of hydrochloric acid (1+1), and heat to decompose. Next, little by little add 5mL of hydrogen peroxide, heat to oxidize the iron, etc., and continue to boil until the excess hydrogen peroxide is decomposed. After cooling, wash the bottom of the watch glass with warm water, and remove the watch glass. Filter the solution using type 5B filter paper, and wash with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid in a 200mL beaker, heat gently until the volume is concentrated to 30mL, and store this as the main sample liquid.

As for the remaining undissolved material, transfer it along with the filter paper to a platinum crucible, and after drying, heat strongly until the paper turns to ash, and then cool to ambient temperature. Moisten the remaining material with 2 or 3 drops of sulfuric acid, add 5mL of hydrofluoric acid, and heat gently until the silicon dioxide and sulfuric acid are volatilized. Add 1g of sodium disulfate, cover and heat gradually at first, raising the temperature gradually to a dark red heat until the remaining material becomes molten. After cooling to ambient temperature, add a small amount of warm water to the platinum crucible, heat gently to dissolve all the soluble material, and combine with the stored main sample liquid. Wash the platinum crucible with a small amount of water, and combine wash liquid with the main sample liquid. Using water, transfer the solution to a 100mL volumetric flask, accurately add 10mL of Al solution (12mg Al/mL), and bring up to volume with water.

Note: Al solution (12mg Al/mL) : Dissolve 110g of aluminum chloride • 6H2O in water and bring volume to 1 liter using water.

### Ti II (Samples difficult to decompose using hydrochloric acid)

Weigh out 1.0g of sample to the nearest 0.001g, and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the white perchloric acid fumes are generated for 5 - 6 minutes. After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with warm water, and remove the watch glass. The rest of the procedure is the same as that described for Ti I.

### V

Weigh out 1.0g of sample (containing 0.005% - 0.20% of V) or 0.20g of sample (containing 0.20% - 1.0% of Mo) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. Add 15mL of perchloric acid, and heat continuously until concentrated to the point that the white perchloric acid fumes are generated. After cooling, add 10mL of hydrochloric acid , heat to dissolve the salts and add 20mL of water. Wash the bottom of the watch glass with water, and remove the watch glass. Wash the bottom of the watch glass with water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remainder. Using water, transfer the solution to a 100mL volumetric flask, accurately add 10 mL of Al solution (20mg Al/mL), cool to ambient temperature, and bring to volume with water.

Note: Al solution (20mg Al/mL) : Dissolve 180g of aluminum chloride •6H20 in water, and bring volume to 1 liter using water.

l Zn I (Samples easily decomposed with mixed acid)

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. The rest of the procedure is the same as that described for Cu I.

l Zn II (Samples difficult to decompose using mixed acid)

Weigh out 1.0g of sample to the nearest 0.001g and transfer to a 200mL beaker. The rest of the procedure is the same as that described for Co II.

b) Iron Separation Method

l Al

Weigh out 2.0g of sample to the nearest 0.001g and transfer to a 300mL quartz beaker. Cover with a quartz watch glass, add 30mL of aqua regia, and heat gently to decompose. Add 25mL of perchloric acid, heat continuously until the white perchloric acid fumes are generated, and then continue heating until the perchloric acid fumes form condensate on the inside surface of the beaker for approximately 10 minutes (For samples containing a large percentage of chromium, little by little add small amounts of hydrochloric acid, and repeat the same procedure of heating to generate the white perchloric acid fumes to volatilize most of the chromium.). After cooling, add approximately 30mL of water to dissolve the salts, wash the bottom of the watch glass with warm water, and remove the watch glass. Filter the solution through filter paper (type 5C), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper, with the filtrate and wash liquid being received in a 300mL beaker. Save the remaining undissolved material.

Heat the filtrate and wash liquid, concentrating it until the white perchloric acid fumes begin to be generated, and then cool to ambient temperature. Add 10mL of hydrochloric acid (10+6) to dissolve the salts, and using 30mL of hydrochloric acid (10+6), transfer the solution to a 200mL separatory funnel. Add 50mL of 4-methyl-2-pentanone (MIBK), shake for 1 minute to mix, and after setting aside to allow formation of 2 separate layers, transfer the bottom aqueous phase to a separate 100mL separatory funnel. Add 10mL of hydrochloric acid (10+6) to the organic phase, shake for 30 seconds to mix, and after setting aside to allow formation of 2 separate layers, combine the aqueous phase with that in the above-mentioned 100mL separatory funnel. Add 25mL of MIBK to the aqueous phase, shake for 30 seconds to mix, and after setting aside to allow formation of 2 separate layers, transfer the aqueous phase to the above-mentioned 300mL quartz beaker. Discard the organic phase. Gently heat the solution to volatilize the dissolved MIBK, and continue heating until the liquid volume is concentrated to about 20mL. Add 5mL of nitric acid, heat again until the white perchloric acid fumes are generated, and continue heating until the liquid volume is concentrated to about 2 - 3mL. Store this as the main sample liquid.

As for the remaining undissolved material, transfer it along with the filter paper to a platinum crucible (No. 30), and after drying, heat strongly until the paper turns to ash, and then cool to ambient temperature. Moisten the remaining material with 2 or 3 drops of sulfuric acid (1+1), add 5mL of hydrofluoric acid, and heat gently until the silicon dioxide and sulfuric acid are volatilized. After cooling, add 1g of sodium disulfide, cover and heat gradually at first, raising the temperature gradually to a dark red heat until the remaining material becomes molten. After cooling, add 10mL of hydrochloric acid (1+3) to the platinum crucible, heat gently to dissolve all the soluble material, and combine with the stored main sample liquid. Wash the platinum crucible with a small amount of water, and combine wash liquid with the main sample liquid. Using water, transfer the solution to a 50mL volumetric flask, and after cooling to ambient temperature, bring up to volume with water.

c) Iodide Extraction Method

l Bi, Pb, Sb, Sn, Te

Sample weights

Referring to the following table, weigh out the sample according to the percent content of the target element.

| Element | Content (%) | Weight (g) |
|---|---|---|
| Bi | 0.0005 - 0.015 | 0.10 |
| Pb | 0.0005 - 0.010 | 0.10 |
| Sb | 0.0015 - 0.030 | 0.10 |
| | 0.030 - 0.050 | 0.50 |
| Sn | 0.002 - 0.020 | 1.0 |
| | 0.020 - 0.10 | 0.20 |
| Te | 0.0005 - 0.010 | 0.10 |
| | 0.010 - 0.050 | 0.20 |

Preparing Sample Solution

Weigh out sample to the nearest 0.001g, and transfer to a beaker. Cover with a watch glass, add 15mL of aqua regia and heat gently to decompose. After cooling, wash the bottom of the watch glass with water, remove the watch glass, and add a small amount of water. Pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate, wash liquid, and discard the precipitate. Add 5mL of sulfuric acid (1+1), heat gently, and when the salts just begin to extract, transfer the beaker to a low temperature site, and continue heating until the white fumes of sulfuric acid are generated. After cooling to ambient temperature, add 10mL of hydrochloric acid (1+1), and heat slightly to dissolve the salts.

To this solution, add 10mL of L(+) ascorbic acid solution (200g/L), shake well to mix, and set aside for about 5 minutes. Using a small amount of water, transfer the solution to a 100mL separatory funnel, add 10mL of potassium iodide solution, and bring the volume of the solution to approximately 50mL using water. Accurately add 10mL of TOPO-4-methyl-2-pentanone solution, shake vigorously to mix for 30 seconds, set aside to allow separation into 2 distinct layers, discard the lower layer, and pass the organic phase through dry filter paper (type 5C) into a container equipped with a stopper.

Notes:

(1) L(+) ascorbic acid solution (200g/L) : Dissolve 20g of L(+) ascorbic acid in water, and bring volume to 100mL. (Prepare at each new usage)

(2) Potassium iodide solution : Dissolve 41.5g of potassium iodide and 15g of L(+) ascorbic acid in approximately 50mL of warm water, add 30mL of hydrochloric acid (1+1), and bring total volume to 100mL using water. (In the case of Bi, 100g of potassium iodide is dissolved in 1 liter of water. Prepare at each new usage.)

(3) TOPO-4-methyl-2-pentanone solution : Dissolve 1g of TOPO ($C_{24}H_{51}OP$) in 100mL of 4-methyl-2-pentanone solution.

d) Tetrahexyl ammonium iodide • trioctylamine extraction

I Zn

Weigh out 0.5g of sample (containing 0.0005% - 0.0030% of Zn) or 0.25g of sample (containing 0.0030% - 0.0060% of Zn) to the nearest 0.001g and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of aqua regia, and heat gently to decompose. After cooling, wash the bottom of the watch glass with water, and remove the watch glass. Add a small amount of water, pass the solution through filter paper (type 5A), and wash the filter paper with warm hydrochloric acid (2+100) and warm water until there is no sign of the yellow colored iron chloride (III) on the filter paper. Combine the filtrate and wash liquid, and discard the remaining precipitate. Add 10mL of sulfuric acid (1+1), heat gently, and when the salts just begin to extract, transfer the beaker to a low temperature site, and continue heating until the white fumes of sulfuric acid are generated for 3 - 5 minutes. After cooling to ambient temperature, add 25mL of hydrochloric acid (1+1), heat slightly to dissolve the salts and cool to ambient temperature.

To this solution, after adding about 15mL of water, add 2g of L(+) ascorbic acid, and shake well to mix and reduce the iron (III), etc. Using a small amount of water, transfer the solution to a 200mL separatory funnel, and bring the volume of the solution to approximately 50mL using water. Accurately add 10mL of tetrahexyl ammonium iodide-4-methyl-2-pentanone solution, shake vigorously to mix for 30 seconds, set aside to allow separation into 2 distinct layers, discard the lower aqueous layer, and pass the organic phase through dry filter paper (type 5A) into a container equipped with a stopper.

Note:

Tetrahexyl ammonium iodide-4-methyl-2-pentanone solution : Dissolve 5g of tetra-n-hexyl ammonium [CH3 (CH2)5]4NI in 4-methyl-2-pentanone, and to this, add 30mL of tri-n-octyl amine [CH3 (CH2)7]3N, and bring the total volume to 1000mL using 4-methyl-2-pentanone.

I P I (samples easily decomposed using nitric acid)

Weigh out 1.0g of sample (containing 0.0003% - 0.0050% of P) or 0.50g of sample (containing 0.0050% - 0.010% of P) and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of nitric acid (1+1), and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the thick white fumes of perchloric acid are generated for 5 - 6 minutes. After cooling, add 30mL of warm water to dissolve the salts. To this solution, add 2mL of hydrogen peroxide to reduce the chromium, boil to decompose the excess hydrogen peroxide, and cool. Wash the bottom of the watch glass with warm water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper 5 - 6 times alternately with warm perchloric acid (2+100) and warm water. Transfer the filtrate and wash liquid to a 100mL volumetric flask using water, and after cooling to ambient temperature, bring up to volume with water.

Transfer a 20mL aliquot of this solution to a 100mL separatory funnel, add 8mL of perchloric acid and enough water to bring the volume of the solution to 30mL, and then shake to mix. To this, add 10mL of ammonium molybdate (IV) tetrahydrate solution A, shake well to mix, set aside to allow separation into 2 distinct layers, discard the lower layer, and pass the organic phase through dry filter paper (type 5A) into a container equipped with a stopper.

Note:

Ammonium molybdate (IV) tetrahydrate solution A : Dissolve 100g of ammonium-7-molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\bullet 4H2O]$ in approximately 900mL of warm water, cool to ambient temperature and add water to bring the total liquid volume to 1 liter. Filter out any precipitate, which may be present.

- P II (samples difficult to decompose using nitric acid)

Weigh out the sample as described for P I, and transfer to a 200mL beaker. Cover with a watch glass, add 15mL of mixed acid (1 part hydrochloric acid, 1 part nitric acid), and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the thick white fumes of perchloric acid are generated for 5-6 minutes. After cooling, add approximately 30mL of warm water to dissolve the salts. The rest of the procedure is the same as that described for P I from the point of adding 2mL of hydrogen peroxide.

- P III (samples containing vanadium)

Weigh out the sample as described for P I, and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of nitric acid, and heat gently to decompose. Add 15mL of perchloric acid, and continue heating until the thick white fumes of perchloric acid are generated for 5-6 minutes. After cooling, add approximately 30mL of warm water to dissolve the salts, add 2mL of hydrogen peroxide to reduce the chromium, and boil to decompose the excess hydrogen peroxide. After cooling, add 5mL of ammonium iron (II) sulfate solution to reduce the vanadium. Wash the bottom of the watch glass with warm water, and remove the watch glass. The rest of the procedure is the same as that for P I from the point of filtering the solution using type 5A filter paper.

Note:

Ammonium iron (II) sulfate solution : Add 70mL of water and 2mL of hydrogen peroxide to 4g of ammonium iron (II) sulfate hexahydrate [$FeSO_4\ (NH_4)_2SO_4\bullet 6H_2O$] to dissolve, and bring volume to 100mL using water.

- P IV (samples containing niobium, titanium, zirconium and arsenic)

Weigh out the sample as described for P I, and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of nitric acid (1+1), and heat gently over a water bath to decompose. Add 15mL of perchloric acid, and continue heating until the thick white fumes of perchloric acid are generated for 5-6 minutes. After cooling, add 3mL of hydrofluoric acid and enough water to bring the liquid volume to about 70mL. After heating to dissolve the salts, add 3g of boric acid, and shake well to dissolve. To this solution, add 2mL of hydrogen peroxide to reduce the chromium, boil to decompose the excess hydrogen peroxide, and cool. Wash the bottom of the watch glass with warm water, and remove the watch glass. Pass the solution through filter paper (type 5A), and wash the filter paper 5 - 6 times alternately with warm perchloric acid (2+100) and warm water. Transfer the filtrate and wash liquid to a 100mL volumetric flask using water, and after cooling to ambient temperature, bring up to volume with water.

Transfer a 10mL aliquot of this solution to a 100mL separatory funnel, add 17mL of nitric acid, 5mL of 6-ammonium-7-molybdate solution B and enough water to bring the volume of the solution to 35mL, and then shake to mix. Set aside for approximately 10 minutes, accurately add 10mL of isobutyl acetate, and shake vigorously for 1 minute to mix. After setting aside to allow separation into 2 distinct layers, discard the lower layer, and pass the organic phase through dry filter paper (type 5A) into a container equipped with a stopper.

Note:

Ammonium molybdate (IV) tetrahydrate solution B : Dissolve 240g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\bullet 4H2O]$ in approximately 900mL of warm water, cool to ambient temperature and add water to bring the total liquid volume to 1 liter. Filter out any precipitate, which may be present.

17.1.2 Flame Atomic Absorption Method

a) Target Elements and Quantitation Range

| Element | Content (%) | Quantitation Method |
|---|---|---|
| Al | ≥0.005, ≤0.10<br>≥0.001, ≤0.010 | Direct acid decomposition<br>Iron separation |
| Bi | ≥0.0005, ≤0.015 | Iodide extraction |
| Ca | ≥0.0005, ≤0.010 | Direct acid decomposition |
| Co | ≥0.01, ≤0.50 | Direct acid decomposition |
| Cr | ≥0.002, ≤2.0 | Direct acid decomposition |
| Cu | ≥0.003, ≤1.0 | Direct acid decomposition |
| Mg | ≥0.001, ≤0.10 | Direct acid decomposition |
| Mn | ≥0.003, ≤2.0 | Direct acid decomposition |
| Mo | ≥0.01, ≤1.0 | Direct acid decomposition |
| Ni | ≥0.003, ≤1.0 | Direct acid decomposition |
| P | ≥0.0003, ≤0.010 | Molybdophosphoric acid extraction |
| Pb | ≥0.01, ≤3.0<br>≥0.0005, ≤0.010 | Direct acid decomposition<br>Iodide extraction |
| Sb | ≥0.0015, ≤0.050 | Iodide extraction |
| Sn | ≥0.002, ≤0.10 | Iodide extraction |
| Te | ≥0.0005, ≤0.050 | Iodide extraction |
| Ti | ≥0.01, ≤0.50 | Direct acid decomposition |
| V | ≥0.005, ≤1.0 | Direct acid decomposition |
| Zn | ≥0.005, ≤0.025<br>≥0.0005, ≤0.0060 | Direct acid decomposition<br>Tetrahexyl ammonium iodide • trioctylamine extraction |

b) Measurement Procedure

Measurements are performed according to the following procedures. For the lamp current, slit width and flame conditions, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

I Al I (Direct acid decomposition)

Reagents

(1) Al standard solution (100µg Al/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Al or with as little Al as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Al I and Al II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Al standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Al standard solution (100µg Al/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Al I or Al II.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 1 - 10µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

I Al II (Iron separation)

Reagents

(1) Al standard solution (20µg Al/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Same reagent as described in Al I Reagent (2)

Procedure

(1) The sample solution prepared according to the pretreatment described in b) Al is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Al standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 300mL beakers, and accurately weigh out and transfer to each 2.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Al standard solution (20µg Al/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in b) Al.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 0.4 - 4µg/mL |

Measurement conditions Refer to Cookbook Section 3, Paragraph 6.4, 2)

I Bi

Reagents

(1) Bi standard solution (15µg Bi/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no BI or with as little Bi as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in c) Bi, Pb, Sb, Sn and Te is measured as is.

For the blank test, the solution used for diluting standards is measured as is without adding any Bi standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Bi standard solution (15µg Bi/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in c) Bi, Pb, Sb, Sn and Te.

Measurement

| | |
|---|---|
| Measurement wavelength | 223.1nm |
| Calibration curve concentration range | 1.5 - 15µg/mL |

Measurement conditions

| | |
|---|---|
| Lamp current | 10mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | $C_2H_2$ 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

I Ca

Reagents

(1) Ca standard solution (20µg Ca/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Ca or with as little Ca as possible, with a known percent content.

(3) La solution (50mg La/mL) : Same as described in Note for Ca under sample pretreatment procedure a)

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Ca is measured as is.

For the blank test, the solution used for diluting standards is measured as is without adding any Ca standard solution, and the

result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 2.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Ca standard solution (20µg Ca/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Ca.

Measurement

| | |
|---|---|
| Measurement wavelength | 422.7nm |
| Calibration curve concentration range | 0.2 - 2µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 10) |

**I** Co

Reagents

(1) Co standard solution (100µg Co/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Co or with as little Co as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Co I or Co II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Co standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Co content is 0.01 - 0.10%) or 2.0g of Fe (when Co content is 0.10 - 0.50%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Co standard solution (100µg Co/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Co I or Co II.

Measurement

| | |
|---|---|
| Measurement wavelength | 240.7nm |
| Calibration curve concentration range | 1-10µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 12) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

**I** Cr

Reagents

(1) Cr standard solution (400µg Co/mL)

(2) Cr standard solution (100µg Co/mL)

For (1) and (2), refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(3) Fe : Use Fe with as high purity as possible, containing either no Cr or with as little Cr as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Cr I or Cr II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Cr standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Cr content is 0.002 - 0.10%) or 2.0g of Fe (when Cr content is 0.10 - 2.0%). When the Cr content is 0.002 - 0.50%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Cr standard solution (100µg Cr/mL) to the seven beakers, respectively, and when the Cr content is 0.5 - 2.0%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Cr standard solution (400µg Cr/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Cr I or Cr II.

Measurement

| | |
|---|---|
| Measurement wavelength | 357.9nm (Cr content 0.002 - 0.50%) |
| | 425.4nm (Cr content 0.50 - 2.0%) |
| Calibration curve concentration range | 1-10µg/mL (Cr content 0.002 - 0.50%) |
| | 4-40µg/mL (Cr content 0.50 - 2.0%) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 13) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

**I** Cu

Reagents

(1) Cu standard solution (200µg Cu/mL)

(2) Cu standard solution (100µg Cu/mL)

For (1) and (2), refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(3) Fe : Use Fe with as high purity as possible, containing either no Cu or with as little Cu as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Cu I or Cu II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Cu standard solution, and the

result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Cu content is 0.003 - 0.10%) or 0.5g of Fe (when Cu content is 0.10 - 1.0%). When the Cu content is 0.003 - 0.10%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Cu standard solution (100µg Cu/mL) to the seven beakers, respectively, and when the Cu content is 0.10 - 1.0%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Cu standard solution (200µg Cu/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Cu I or Cu II.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.8nm (Cu content 0.003 - 0.10%) |
| | 327.4nm (Cu content 0.10 - 1.0%) |
| Calibration curve concentration range | 1-10µg/mL (Cu content 0.003 - 0.10%) |
| | 2-20µg/mL (Cu content 0.10 - 1.0%) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 15) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

**I** Mg

Reagents

(1) Mg standard solution (20µg Mg/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Mg or with as little Mg as possible, with a known percent content.

(3) La solution (50mg La/mL) : Same as described in Note for Ca under sample pretreatment procedure a)

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Mg is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Mg standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 0.5g of Fe (when Mg content is 0.001 - 0.040%) or 0.20g of Fe (when Mg content is 0.040 - 0.10%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Mg standard solution (20µg Mg/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Mg.

Measurement

| | |
|---|---|
| Measurement wavelength | 285.2nm |
| Calibration curve concentration range | 0.08-0.8µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 21) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### I Mn

Reagents

(1) Mn standard solution (400µg Mn/mL)
(2) Mn standard solution (50µg Mn/mL)
(3) Mn standard solution (10µg Mn/mL)
For (1) - (3), refer to Cookbook Section 2, Paragraph 3 Preparing Standards
(4) Fe : Use Fe with as high purity as possible, containing either no Mn or with as little Mn as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Mn is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Mn standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Mn content is 0.003 - 0.010%) or 0.5g of Fe (when Mn content is 0.010 - 0.10%) or 0.2g of Fe (when Mn content is 0.10 - 2.0%). When the Mn content is 0.003 - 0.010%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Mn standard solution (10µg Mn/mL) to the seven beakers, respectively. When the Mn content is 0.010 - 0.10%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Mn standard solution (50µg Mn/mL) to the seven beakers, respectively. When the Mn content is 0.10 - 0.50%, accurately add 0, 2, 4, 8, 12, 16 and 20mL of Mn standard solution (50µg Mn/mL) to the seven beakers, respectively, and when the Mn content is 0.50 - 2.0%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Mn standard solution (400µg Mn/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Mn.

Measurement

| | |
|---|---|
| Measurement wavelength | 279.5nm (Mn content 0.003 - 0.50%)<br>403.1nm (Mn content 0.50 - 2.0%) |
| Calibration curve concentration range | 0.1-1.0µg/mL (Mn content 0.003 - 0.010%)<br>0.5-5µg/mL (Mn content 0.010 - 0.1%)<br>1-10µg/mL (Mn content 0.10 - 0.50%)<br>4-40µg/mL (Mn content 0.50 - 2.0%) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 22) |

Note:
If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### I Mo

Reagents

(1) Mo standard solution (500µg Mo/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Mo or with as little Mo as possible, with a known percent content.

(3) Al solution (12mg Al/mL) : Same as described under Note of Sample Pretreatment a) Mo I

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Mo I, Mo II or Mo III is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Mo standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Mo content is 0.01 - 0.50%) or 0.50g of Fe (when Mo content is 0.50 - 1.0%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Mo standard solution (500µg Mo/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Mo I, Mo II or Mo III.

Measurement

| | |
|---|---|
| Measurement wavelength | 313.3nm |
| Calibration curve concentration range | 5-50µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 23) |

I Ni

Reagents

(1) Ni standard solution (500µg Mn/mL)

(2) Ni standard solution (100µg Mn/mL)

For (1), (2), refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(3) Fe : Use Fe with as high purity as possible, containing either no Ni or with as little Ni as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Ni I or Ni II is measured as is.
For the blank test, the solution used for diluting standards is measured as is without adding any Ni standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Ni content is 0.003 - 0.10%) or 0.50g of Fe (when Ni content is 0.10 - 1.0%). When the Ni content is 0.003 - 0.10%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Ni standard solution (100µg Ni/mL) to the seven beakers, respectively, and when the Ni content is 0.10 - 1.0%, accurately add 0, 1, 2, 4, 6, 8 and 10mL of Ni standard solution (500µg Ni/mL) to the seven beakers, respectively. Then perform the same sample pretreatment procedure as described in a) Ni I or Ni II.

Measurement

| | |
|---|---|
| Measurement wavelength | 232.0nm (Ni content 0.003 - 0.10%)<br>352.5nm (Ni content 0.10 - 1.0%) |
| Calibration curve concentration range | 1-10µg/mL (Ni content 0.003 - 0.10%)<br>5-50µg/mL (Ni content 0.10 - 1.0%) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 25) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

I P

Reagents

(1) P standard solution (5µg P/mL) : After drying potassium dihydrogenphosphate at 110°C for approximately 1 hour, cool to ambient temperature in a desiccator, and then weigh out 0.1098g and transfer to a 300mL beaker. Cover with a watch glass, add approximately 100mL of water to dissolve, wash the bottom of the watch glass with water, and remove the watch glass. Transfer the solution to a 1000mL volumetric flask using water, and bring up to volume with water. This will serve as the source solution (25µg P/mL). Whenever this source solution is used, dilute it by a factor of 5 to prepare the P standard solution.

(2) Fe : Use Fe with as high purity as possible, containing either no P or with as little P as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in e) P I, P II, P III or P IV is measured as is.

For the blank test, the solution used for diluting standards is measured as is without adding any P standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when P content is 0.003 - 0.10%) or 0.50g of Fe (when P content is 0.005 - 0.01%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of P standard solution (5µg P/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in e) P I, P II, P III or P IV.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.6nm |
| Calibration curve concentration range | 0.25-2.5µg/mL |

I Pb I (Direct acid decomposition method)

Reagents

(1) Pb standard solution (300µg Pb/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Pb or with as little Pb as possible, with a

known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Pb is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Pb standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Pb standard solution (300µg Pb/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Pb.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Calibration curve concentration range | 3-30µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 27) |

**I** Pb II (Iodide extraction method)

Reagents

(1) Pb standard solution (10µg Pb/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Same as described for Pb I

Procedure

(1) Same as that described for Bi

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Pb standard solution (10µg Pb/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in c) Bi, Pb, Sb, Sn, Te.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Calibration curve concentration range | 1 - 10µg/ml |
| Measurement conditions | |
| Lamp current | 10mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | C2H2 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

**I** Sb

Reagents

(1) Sb standard solution (30µg Sb/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Sb or with as little Sb as possible, with a known percent content.

Procedure

(1) Same as that described for Bi

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Sb content is 0.0015 - 0.030%) or 0.50g of Fe (when Sb content is 0.030 - 0.050%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Sb standard solution (30µg Sb/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in c) Bi, Pb, Sb, Sn, Te.

Measurement

| | |
|---|---|
| Measurement wavelength | 217.6nm |
| Calibration curve concentration range | 3 - 30µg/ml |
| Measurement conditions | |
| Lamp current | 13mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | C2H2 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

**I** Sn

Reagents

(1) Sn standard solution (20µg Sn/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Sn or with as little Sn as possible, with a known percent content.

Procedure

(1) Same as that described for Bi

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Sn content is 0.002 - 0.020%) or 0.20g of Fe (when Sn content is 0.020 - 0.10%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Sn standard solution (30µg Sb/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in c) Bi, Pb, Sb, Sn, Te.

Measurement

| | |
|---|---|
| Measurement wavelength | 286.3nm |
| Calibration curve concentration range | 2 - 20µg/ml |
| Measurement conditions | |
| Lamp current | 10mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | C2H2 1.2L/min |

I Te

Reagents

(1) Te standard solution (10µg Te/mL) : Weigh out 0.100g of Te (≥99.9%) and transfer to a 200mL beaker. Cover with a watch glass, add 20mL of hydrochloric acid and 10mL of nitric acid, heat gently to decompose, and continue heating to volatilize the nitric oxide, etc. After cooling to ambient temperature, wash the bottom of the watch glass with water, and remove the watch glass. Transfer the solution to a 1000mL volumetric flask using hydrochloric acid (1+1), and bring up to volume using hydrochloric acid (1+1). This will serve as the source solution (100µg Te/mL). To prepare the Te standard solution, take a 20mL aliquot of this source solution, add 20mL of hydrochloric acid (1+1), and dilute this accurately to 200mL using water.

(2) Fe : Use Fe with as high purity as possible, containing either no Te or with as little Te as possible, with a known percent content.

Procedure

(1) Same as that described for Bi

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when Te content is 0.0005 - 0.010%) or 0.50g of Fe (when Te content is 0.010 - 0.050%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Te standard solution (10µg Te/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in c) Bi, Pb, Sb, Sn, Te.

Measurement

| | |
|---|---|
| Measurement wavelength | 214.3nm |
| Calibration curve concentration range | 1 - 10µg/ml |
| Measurement conditions | |
| Lamp current | 14mA |
| Slit width | 0.2nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |

Fuel gas flow rate C2H2 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.)

**I** Ti

Reagents

(1) Ti standard solution (500µg Ti/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Ti or with as little Ti as possible, with a known percent content.

(3) Al solution (12mg Al/mL) : Same as described under Note of Sample Pretreatment a) Ti I

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Ti I or Ti II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Ti standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Ti standard solution (500µg Ti/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Ti I, or Ti II.

Measurement

| | |
|---|---|
| Measurement wavelength | 364.3nm |
| Calibration curve concentration range | 5-50µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 41) |

**I** V

Reagents

(1) V standard solution (200µg V/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no V or with as little V as possible, with a known percent content.

(3) Al solution (20mg Al/mL) : Same as described under Note of Sample Pretreatment a) V

Procedure

(1) The sample solution prepared according to the pretreatment described in a) V is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any V standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe (when V content is 0.005 - 0.020%) or 0.20g of Fe (when V content is 0.020 - 1.0%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of V standard solution (200µg V/mL) to the seven beakers,

respectively, and then perform the same sample pretreatment procedure as described in a) V.

Measurement

| | |
|---|---|
| Measurement wavelength | 318.4nm |
| Calibration curve concentration range | 2-20µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 43) |

I Zn I (Direct acid decomposition method)

Reagents

(1) Zn standard solution (25µg Zn/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Use Fe with as high purity as possible, containing either no Zn or with as little Zn as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment described in a) Zn I or Zn II is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Zn standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 1.0g of Fe. Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Zn standard solution (25µg Pb/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in a) Zn I or Zn II.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Calibration curve concentration range | 0.25-2.5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 44) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

I Zn II (Tetrahexyl ammonium iodide • trioctylamine extraction)

Reagents

(1) Zn standard solution (1.5µg Zn/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe : Same as described for Zn I

Procedure

(1) The sample solution prepared according to the pretreatment described in d) Zn is measured as is. For the blank test, the solution used for diluting standards is measured as is without adding any Zn standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) For the standard solutions to be used for generating a calibration curve, prepare seven 200mL beakers, and accurately weigh out and transfer to each 0.5g of Fe (when Zn content is 0.0005 - 0.0030%) or 0.25g of Fe (when Zn content

is 0.0030 - 0.0060%). Accurately add 0, 1, 2, 4, 6, 8 and 10mL of Zn standard solution (1.5µg Zn/mL) to the seven beakers, respectively, and then perform the same sample pretreatment procedure as described in d) Zn.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Calibration curve concentration range | 0.15-1.5µg/ml |
| Measurement conditions | |
| Lamp current | 8mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Support gas | Air |
| Fuel gas flow rate | $C_2H_2$ 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

## 17.2 Ferro Alloy Analysis Method

Reference Materials

Japan Industrial Standard

| | |
|---|---|
| Ferrosilicon Analysis Method | JIS G 1312 |
| Ferromolybdenum Analysis Method | JIS G 1317 |
| Ferrovanadium Analysis Method | JIS G 1318 |
| Metallic Silicon Analysis Method | JIS G 1322 |
| Metallic Chromium Analysis Method | JIS G 1323 |
| Ferronickel Analysis Method | JIS G 1326 |
| Ferroniobium Analysis Method | JIS G 1328 |

### 17.2.1 Sample Pretreatment

a) Al (ferrosilicon)

Weigh out 1.0g of sample to the nearest 1mg, transfer to a platinum dish (No. 100), add 10mL of nitric acid (1+1), and cover. Drip 10mL of hydrofluoric acid onto the dish contents to decompose the sample, add 10mL of perchloric acid, heat on a sand bath to generate the white fumes of perchloric acid, and continue heating until the liquid volume is concentrated down to approximately 3mL. After cooling, add approximately 30mL of warm water, heat to dissolve the soluble salts, cool to ambient temperature, transfer to a 100mL volumetric flask, and bring to volume with water.

b) Al (ferromolybdenum, ferrovanadium)

Weigh out 1.0g of sample to the nearest 1mg, transfer to a 300mL beaker and cover with a watch glass. Add 20mL of hydrochloric acid (1+1) and 10mL of nitric acid (1+1), heat to decompose, and taking care not to allow boiling, heat to dryness. After cooling, add 20mL of hydrochloric acid (1+1), heat to dissolve the soluble salts, add approximately 30mL of warm water, and filter using type 6 filter paper. Transfer any residue adhering to the beaker to the filter paper by scraping with a policeman, and wash with the surface of the filter paper with warm hydrochloric acid (1+50) until there is no sign of the iron ion reaction, and then wash away the acid with warm water, collecting all of the filtrate and wash liquid in 300mL beaker. Concentrate the liquid in the beaker to approximately 50mL through vaporization, and store this as a source solution.

Transfer the residue, which is on the filter paper along with the filter paper to a platinum crucible (No. 30), and heat gradually to ash. After cooling, add 2-3 drops of sulfuric acid (1+1) to moisten the residue, add 3-5mL of hydrofluoric acid, and while carefully heating to avoid loss due to splattering, volatilize the silicon dioxide and sulfuric acid. Add to the crucible 1.0g of potassium pyrosulfate, and gradually increase the temperature to about 700°C to completely melt the residue. After cooling, place the crucible into the beaker containing the above-mentioned stored source solution, gradually heat to dissolve the fused substance, wash the crucible water, and remove the crucible from the beaker. Cool the solution to ambient temperature, transfer it to a 100mL volumetric flask, and bring to volume with water.

c) Al, Ca, Fe (metallic silicon)

Weigh out 1.0g of sample to the nearest 1mg, transfer to a platinum dish (No. 100), add 10mL of nitric acid (1+1), and cover. Drip 5mL of hydrofluoric acid onto the dish contents to decompose the sample. If this reaction become violent, decompose while cooling with water. Add 5mL of perchloric acid, heat on a sand bath to generate the white fumes of perchloric acid, and continue heating until the liquid volume is concentrated down to approximately 2mL. After cooling, add approximately 30mL of warm water, heat to dissolve the soluble salts, cool to ambient temperature, transfer to a 100mL volumetric flask, and bring to volume with water.

d) Al, Fe (metallic chromium)

Weigh out 1.0g of sample to the nearest 1mg, transfer to a 500mL beaker, and cover with a watch glass. Add 15mL of perchloric acid to decompose, and heat until the white fumes of perchloric acid are generated for about 10 minutes. After cooling, add approximately 50mL of warm water to dissolve the soluble salts, filter through type 5A filter paper into a 100mL volumetric flask, wash with warm water, and bring to volume with water.

e) Al, Si, Sn (ferroniobium)

Weigh out 0.20g of sample to the nearest 0.1mg, transfer to a 300mL polyethylene beaker, and cover. Add 10mL of hydrofluoric acid (1+1), set aside at ambient temperature for 1-2 hours to allow most of the sample to decompose, and add a few drops (less than 1mL) of nitric acid to completely decompose the sample (for samples which are difficult to decompose, it is acceptable to heat up to 70°C). Transfer this solution to a 100mL polyethylene volumetric flask, and bring to volume with water.

f) Co, Cu, Mn (ferronickel)

Weigh out 0.50g of sample to the nearest 0.1mg, transfer to a 300mL beaker, and cover with a watch glass. Add 20mL of nitric acid (1+1), gradually heat to decompose, and then add 20mL of perchloric acid. Heat continuously until the total liquid volume is concentrated to about 10mL. After cooling, add 16mL of hydrochloric acid (1+1), heat to dissolve the soluble salts, filter through type 5B filter paper, and wash sufficiently with warm water. After cooling both filtrate and wash liquid to ambient temperature, transfer to a 100mL volumetric flask, and bring to volume with water.

g) Cr (ferronickel)

Weigh out 0.50g of sample to the nearest 0.1mg, transfer to a 300mL beaker, and cover with a watch glass. Add 20mL of nitric acid (1+1), gradually heat to decompose, and then add 20mL of perchloric acid. Heat continuously until the white fumes of perchloric acid begin to be generated, and maintain the heating temperature at 200°C until the total liquid volume is concentrated to about 10mL. After cooling, add 16mL of hydrochloric acid (1+1) and 20mL of warm water, heat to dissolve the soluble salts, filter through type 5B filter paper, and wash sufficiently with warm water. After cooling both filtrate and wash liquid to ambient temperature, transfer to a 100mL volumetric flask, add 10mL of potassium disulfate solution (100g/L), and bring to volume with water.

h) Cu (ferromolybdenum)

Weigh out 0.50g of sample to the nearest 0.1mg, transfer to a 200mL beaker, and cover with a watch glass. Add 10mL of sulfuric acid (1+1) and 20mL of nitric acid (1+1), and heat to decompose. Wash the bottom of the watch glass, remove it, and then heat continuously until almost no white fumes are generated. After cooling, add 20mL of hydrochloric acid (1+1), heat to dissolve the soluble salts, filter through type 5A filter paper, and wash sufficiently with warm hydrochloric acid (1+50), collecting both filtrate and wash liquid in a 100mL volumetric flask. Cool to ambient temperature, and bring to volume with water. Discard the residue in the filter paper.

17.2.2 Flame Atomic Absorption Method

a) Target Elements and Quantitation Range

| Element | Content (%) |
|---|---|
| Al | ≤3.0% (ferrosilicon)<br>≤0.2% (ferromolybdenum)<br>≤1.0% (ferrovanadium)<br>≤2.0% (metallic silicon)<br>≤0.3% (metallic chromium)<br>2.5% (ferroniobium) |
| Ca | ≤0.4% |
| Co | 0.01-2.0% |
| Cr | 0.01-2.0% |
| Cu | ≤0.05% (ferromolybdenum)<br>≤0.01% (ferronickel) |
| Fe | ≤1.0% (metallic silicon)<br>≤0.2% (metallic chromium) |
| Mn | ≤0.01% |
| Si | ≤3.0% |
| Sn | ≤3.0% |

### b) Measurement Procedure

Measurement is conducted using the following procedure. For lamp current and slit width, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

### I Al I (ferrosilicon)

Reagents

(1) Al standard solution (500µg Al/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe solution (25mg Fe/mL) : Weigh out 2.5g of pure iron, transfer to a 300mL beaker, add 20mL of perchloric acid, and heat to decompose. Continue heating until the white fumes of perchloric acid are generated. After cooling, add 50mL of warm water, heat to dissolve the soluble salts, and after cooling to ambient temperature, transfer to a 100mL volumetric flask and bring up to volume with water.

Procedure

(1) When the sample contains less than 0.5% of Al, the solution prepared according to pretreatment procedure a) Al may be used as is for measurement. If the sample contains between 0.5% and 3.0% of Al, transfer a 10mL aliquot of the sample solution to a 100mL volumetric flask, bring to volume with water, and use this solution for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Al standard solution, and the result is used to correct subsequent standard and sample measurement values.

To prepare standard solutions for generating a calibration curve, prepare several platinum dishes (No. 100), and transfer into each of these Fe solution (25mg Fe/mL) containing the same amount of Fe as that contained in the sample solution, and to each of these, accurately add Al standard solution (500µg Al/mL) in incrementally increasing volumes from 0 - 10.0mL. Then perform the same procedure as that described in Sample Pretreatment a) Al.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 5 - 50µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

### I Al II (ferromolybdenum)

Reagents

(1) Al standard solution (200µg Al/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Fe solution (20mg Fe/mL) : Weigh out five 1.0g portions of pure iron, transfer each to a 300mL beaker, cover with a watch glass, add 20mL of hydrochloric acid (1+1), and gradually heat to decompose. After cooling, add 5mL of hydrogen peroxide little by little to oxidize the iron, and continue heating to vaporize until a film appears on the surface of the liquid. Add 10mL of hydrochloric acid (2+1) to dissolve the soluble salts, cool to ambient temperature or below and transfer to a 200mL separatory funnel. Wash the inside of the beaker with a small amount of hydrochloric acid (2+1), and combine this wash liquid with the original liquid in the separatory funnel. Add a volume of 4-methyl-2-pentanone (MIBK) which is equal or greater than the solution in the separatory funnel, shake vigorously for about one minute, and set aside to allow formation of 2 separate layers. Discard the lower layer (aqueous phase). Add 10mL of hydrochloric acid (2+1) to the organic phase, shake vigorously for about 30 seconds, set aside to allow formation of 2 separate layers, and discard the aqueous phase. Add 30mL of water to the organic phase, shake vigorously for about 30 seconds, set aside to allow

formation of 2 separate layers, and transfer the aqueous phase to the original beaker. Add a further 10mL of water to the organic phase, shake vigorously for about 30 seconds, and after setting aside to allow formation of 2 separate layers, combine the aqueous phase with the liquid already in the original beaker. Discard the organic phase. Heat the solution to volatilize all of the MIBK, add 5mL of nitric acid, and continue heating to dryness. After cooling, add 20mL of hydrochloric acid (1+1), heat to dissolve the soluble salts, cool to ambient temperature, transfer all of the five solutions to a single 250mL volumetric flask, and bring to volume with water.

(3) Mo solution (approx. 25mg Mo/mL) : Dissolve 23g of ammonium molybdate $[(NH_4)_6Mo_7O_{24}\bullet 4H2O]$ in water, transfer to a 500mL volumetric flask, and bring to volume with water.

(4) Potassium pyrosulfate solution : Weigh 10g of potassium pyrosulfate into a platinum crucible, heat strongly to melt, dissolve in water and bring to 100mL (prepare at each usage).

#### Procedure

(1) The sample solution prepared according to the Sample Pretreatment procedure b) Al is used as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 300mL beakers, and into each add 10mL of Fe solution (20mg Fe/mL) and 10mL of Mo solution (25mg Mo/mL), and to these, accurately add Al standard solution (200µg Al/mL) in incrementally increasing volumes from 0 - 10.0mL. Add 10mL of nitric acid and 10mL of sulfuric acid (1+1), heat until almost no fumes of sulfuric acid are generated, and then cool. Add 20mL of hydrochloric acid (1+1) and 10mL of potassium pyrosulfate solution to dissolve the soluble salts, cool to ambient temperature, transfer to a 100mL volumetric flask, and bring to volume with water.

#### Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 2 - 20µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

### I Al III (ferrovanadium)

#### Reagents

(1) Al standard solution (1000µg Al/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Background solution : Weigh out 3.50g of iron (containing a maximum of 0.001% Al) and 6.5g of V (containing a maximum of 0.001% Al), transfer these to a 500mL beaker, cover with a watch glass, add 100mL of hydrochloric acid (1+1) and 20mL of nitric acid (1+1), and gradually heat to decompose. After cooling to ambient temperature, transfer to a 500mL volumetric flask, and bring to volume with water.

(3) Potassium pyrosulfate solution : Same procedure as described in Reagents Al II

Procedure

(1) The sample solution prepared according to the Sample Pretreatment procedure b) Al is used as is.
For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 300mL beakers. Into each add 50mL of background solution, and to this, accurately add Al standard solution (1000µg Al/mL) in incrementally increasing volumes from 0 - 10.0mL. Add 10mL of hydrochloric acid (1+1), and heat carefully to dryness. After cooling, add 20mL of hydrochloric acid (1+1) and 10mL of potassium pyrosulfate solution, and heat to dissolve the soluble salts. Cool to ambient temperature, transfer to a 100mL volumetric flask, and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 5 - 100µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

I Al IV (metallic silicon)

Reagents

(1) Al standard solution (500µg Al/mL) : Same as that described in Al I, Reagents (1)

(2) Fe solution (1mg Fe/mL) : Weigh out 1.0g of pure iron, transfer to a 300mL beaker and add 10mL of perchloric acid. The rest of the procedure is the same as that described for Al I, from the point of heating to decompose the iron.

Procedure

(1) When the Al content in the sample is 0.5% or less, the sample solution prepared according to the pretreatment procedure described in c) Al, Ca, Fe is measured as is. If the percent content is 0.5-2.0%, transfer a 20mL aliquot of the sample solution to a 100mL volumetric flask, and bring up to volume with water.
For the blank test, the solution used for diluting standards is measured as is without adding any Al standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several platinum dishes (No. 100), and transfer into each of these Fe solution (1mg Fe/mL) containing the same amount of Fe as that contained in the sample solution, and to each of these, accurately add Al standard solution (500µg Al/mL) in incrementally increasing volumes from 0 - 10.0mL. Then perform the same procedure as that described in Sample Pretreatment c) Al, Ca, Fe.

Measurement : Same as for Al I

### I Al V (metallic chromium)

Reagents

(1) Al standard solution (500µg Al/mL) : Same as that described in Al I, Reagents (1)

(2) Electrolytically purified metallic chromium

Procedure

(1) The sample solution prepared according to the pretreatment procedure described in d) Al, Fe is measured as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 500mL beakers, and into each add 1.0g of electrolytically purified chromium. To each of these, accurately add Al standard solution (500µg Al/mL) in incrementally increasing volumes from 0 - 6.0mL (0-3.0mg of Al). The rest of the procedure is the same as that described in sample pretreatment d) Al, Fe, from the point of adding 15mL of perchloric acid and heating to decompose.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 3 - 30µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

### I Al VI (ferroniobium)

Reagents

(1) Al standard solution (500µg Al/mL) : Same as Al I, Reagent (1)

(2) Nb solution (10mg Nb/mL) : Weigh out 1.00g of Nb (purity ≥99.7%), and transfer to a 300mL polyethylene beaker. Add 10mL of water and 5mL of hydrofluoric acid, and then, little by little, drip into the beaker 1mL of nitric acid to decompose the Nb. Transfer this to a 100mL polyethylene volumetric flask, and bring up to volume with water.

(3) Fe solution (10mg Fe/mL) : Weigh out 2.50g of Fe (purity ≥99.9%), and transfer to a 300mL polyethylene beaker. Add 10mL of water and 5mL of hydrofluoric acid, and then, little by little, add 5mL of nitric acid to decompose.. Transfer this to a 250mL polyethylene volumetric flask, and bring up to volume with water.

Procedure

(1) The sample solution prepared according to the pretreatment procedure described in e) Al, Si, Sn is measured as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 100mL polyethylene volumetric flasks, and into each accurately add 13mL of Nb solution (10mg Nb/mL) and 5.5mL of Fe solution (10mg Fe/mL). To each of these, accurately add Al standard solution (500µg Al/mL) in incrementally increasing volumes from 0 - 10.0mL (0-5.0mg of Al), and bring up to volume with water.

Measurement : Same as for Al I

## **I** Ca

### Reagents

(1) Ca standard solution (200µg Ca/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Potassium chloride solution : Dissolve 19.5g of potassium chloride (KCl) in water, and bring volume to 1000mL.

(3) Fe solution (1mg Fe/mL) : Same as Al IV, Reagent (2)

(4) Al solution (1mg Al/mL) : Weigh out 0.10g of Al, transfer to a 200mL beaker, add 10mL of hydrochloric acid (1+1), add 2mL of nitric acid, heat to decompose the Al, add 10mL of perchloric acid, and heat until the white fumes of perchloric acid are generated. After cooling, transfer to a 100mL volumetric flask, and bring to volume with water.

### Procedure

(1) Transfer to a 100mL volumetric flask a 10mL aliquot of the sample solution prepared according to the pretreatment procedure c) Al, Ca, Fe. Add 10mL of potassium chloride solution, and bring to volume with water. Use this solution for measurement.

For the blank test, the solution used for diluting standards is measured as is without adding any Ca standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several platinum dishes (No. 100), and transfer into each of these Fe solution (1mg Fe/mL) and Al solution (1mg Al/mL) containing the same amount of Fe and Al, respectively, as that contained in the sample solution. In addition, to each of these, accurately add Ca standard solution (200µg Ca/mL) in incrementally increasing volumes from 0 - 10.0mL (0-2.0mg of Ca). Then perform the same procedure as that described in sample pretreatment c) Al, Ca, Fe, and use an aliquot prepared in the same way as described in Procedure (1).

### Measurement

| | |
|---|---|
| Measurement wavelength | 422.7nm |
| Calibration curve concentration range | 0.2 - 2µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 10) |

**I** Co

Reagents

(1) Co standard solution (50μg Co/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ni : Use Ni with as high purity as possible, containing either no Co or with as little Co as possible, with a known percent content.

(3) Fe : Use Fe with as high purity as possible, containing either no Co or with as little Co as possible, with a known percent content.

Procedure

(1) When the Co content in the sample is 0.2% or less, the sample solution prepared according to the pretreatment procedure described in f) Co, Cu, Mn is measured as is. If the percent content is 0.2-1.0%, transfer a 20mL aliquot of the sample solution to a 100mL volumetric flask, add 13mL of hydrochloric acid (1+1), and bring up to volume with water. This solution is used for measurement. If the percent content of Co is 1.0 - 2.0%, transfer a 10mL aliquot of the sample solution to a 100mL volumetric flask, add 15mL of hydrochloric acid (1+1), and bring up to volume with water. This solution is used for measurement.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, when the Co content in the sample is 0.2% or less, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment f) Co, Cu, Mn, and to these beakers, accurately add Co standard solution (50μg Co/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Co), and bring to volume with water.

If the Co content in the sample is greater than 0.2%, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment f) Co, Cu, Mn, and after preparing an aliquot according to procedure (1), accurately add to these beakers Co standard solution (50μg Co/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Co), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 240.7nm |
| Calibration curve concentration range | 0.5 - 10μg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 12) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

**I** Cr

Reagents

(1) Cr standard solution (50µg Cr/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ni : Use Ni with as high purity as possible, containing either no Cr or with as little Cr as possible, with a known percent content.

(3) Fe : Use Fe with as high purity as possible, containing either no Cr or with as little Cr as possible, with a known percent content.

Procedure

(1) When the Cr content in the sample is 0.2% or less, the sample solution prepared according to the pretreatment procedure described in g) Cr is measured as is. If the percent content of Cr is 0.2-1.0%, transfer a 20mL aliquot of the sample solution to a 100mL volumetric flask, add 13mL of hydrochloric acid (1+1) and 8mL of sodium disulfate (100g/L), and bring up to volume with water. This solution is used for measurement. If the percent content is 1.0 - 2.0%, transfer a 10mL aliquot of the sample solution to a 100mL volumetric flask, add 15mL of hydrochloric acid (1+1) and 9mL of sodium disulfate (100g/L), and bring up to volume with water. This solution is used for measurement.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, when the Cr content in the sample is 0.2% or less, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment g) Cr, and to these beakers, accurately add Cr standard solution (50µg Cr/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Cr), and bring to volume with water.

If the Cr content in the sample is greater than 0.2%, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment g) Cr, and after preparing an aliquot according to procedure (1), accurately add to these beakers Cr standard solution (50µg Cr/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Cr), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 357.9nm |
| Calibration curve concentration range | 0.5 - 10µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 13) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

## I Cu I (ferromolybdenum)

Reagent

(1) Cu standard solution (500µg Cu/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Copper-free ferric chloride solution (approx. 20mg Fe/mL) : Weigh out five 1.0g portions of pure iron, and transfer each to a 300mL beaker. Add 10mL of hydrochloric acid, cover with a watch glass, and heat gently to decompose. To this solution add 5mL of hydrogen peroxide to oxidize the iron, and heat continuously and carefully to volatilize until dry, without burning the residue. After cooling, add 10mL of hydrochloric acid (10+6) to dissolve the soluble salts, and cool to ambient temperature. Using approximately 20mL of hydrochloric acid (10+6), wash and transfer the solution to a 200mL separatory funnel. Add 30mL of 4-methyl-2-pentanone (MIBK), shake vigorously for about 1 minute, set aside to allow formation of 2 separate layers, and discard the lower layer (aqueous phase). Add 20mL of water to the organic phase, shake vigorously for approximately 1 minute, set aside to allow formation of 2 separate layers, and transfer the lower layer aqueous phase to the original beaker. Add a further 10mL of water to the separatory funnel, shake vigorously for about 1 minute, and after setting aside to allow formation of 2 separate layers, combine the aqueous phase with the liquid already in the original beaker. Discard the organic phase. Heat the solution for about 5 minutes to volatilize almost all of the MIBK, add 5mL of nitric acid, and continue heating to dryness. After cooling, add 20mL of hydrochloric acid (1+1), heat gently to dissolve the soluble salts, cool to ambient temperature, transfer all of the five solutions to a single 250mL volumetric flask, and bring to volume with water.

Procedure

(1) The sample solution prepared according to the pretreatment procedure described in h) Cu is measured as is. For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 100mL volumetric flasks, into each of these transfer 10mL of copper-free ferric chloride solution (approx. 20mg Fe/mL) (approx. 200mg of Fe), and to these, accurately add Cu standard solution (500µg Cu/mL) in incrementally increasing volumes from 0 - 5.0mL (0 - 2.5mg of Cu), and bring up to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.7nm |
| Calibration curve concentration range | 1 - 25µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 15) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### I Cu II (ferronickel)

Reagents

(1) Cu standard solution (50µg Cu/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ni : Use Ni with as high purity as possible, containing either no Cu or with as little Cu as possible, with a known percent content.

(3) Fe : Use Fe with as high purity as possible, containing either no Cu or with as little Cu as possible, with a known percent content.

Procedure

(1) The sample solution prepared according to the pretreatment procedure described in f) Co, Cu, Mn is measured as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment f) Co, Cu, Mn, and to these beakers, accurately add Cu standard solution (50µg Cu/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Cu), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.7nm |
| Calibration curve concentration range | 0.5 - 10µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 15)Note: |

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### I Fe I (metallic silicon)

Reagents

(1) Fe standard solution (1000µg Fe/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

(1) Transfer to a 100mL volumetric flask 10mL of the sample solution prepared according to the pretreatment procedure described in c) Al, Ca, Fe, and bring up to volume with water.

For the blank test, the solution used for diluting standards is measured as is without adding any Fe standard solution, and the result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several platinum dishes (No. 100), and to these, accurately add Fe standard solution (1000µg Fe/mL) in incrementally increasing volumes from 0 - 5.0mL (0 - 5.0mg of Fe). Perform the same procedure as that described in Sample Pretreatment c) Al, Ca, Fe, and then prepare an aliquot is described in procedure (1).

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |
| Calibration curve concentration range | 0.5 - 5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 16) |

I Fe II (metallic chromium)

Reagents

(1) Fe standard solution (100µg Fe/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Cr solution (10mg Cr/mL) : Weigh out 1.00g of electrolytically purified metallic chromium, and transfer to a 500mL beaker. Cover with a watch glass, add 15mL of perchloric acid, heat to decompose, and continue heating until the white fumes of perchloric acid are generated for about 10 minutes. After cooling, add 50mL of warm water to dissolve the salts, transfer to a 100mL volumetric flask, cool to ambient temperature, and bring to volume with water.

Procedure

(1) Transfer to a 100mL volumetric flask 10mL of the sample solution prepared according to the pretreatment procedure described in d) Al, Fe, and bring up to volume with water.
For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 100mL volumetric flasks, and to each of these, add 10mL of Cr standard solution (10mg Cr/mL). Further, accurately add to these flasks Fe standard solution (100µg Fe/mL) in incrementally increasing volumes from 0 - 2.0mL (0-0.2mg of Fe), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |
| Calibration curve concentration range | 0.2 - 2µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 16) |

I Mn

Reagents

(1) Mn standard solution (50µg Cr/mL) : Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

(2) Ni : Use Ni with as high purity as possible, containing either no Mn or with as little Mn as possible, with a known percent content.

(3) Fe : Use Fe with as high purity as possible, containing either no Mn or with as little Mn as possible, with a known percent content.

Procedure

(1) When the Mn content in the sample is 0.2% or less, the sample solution prepared according to the pretreatment procedure described in f) Co, Cu, Mg is measured as is. If the percent content of Mn is greater than 0.2%, transfer a 20mL aliquot of the sample solution to a 100mL volumetric flask, add 13mL of hydrochloric acid (1+1), and bring up to volume with water.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, when the Mn content in the sample is 0.2% or less, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment f) Co, Cu, Mn, and to these beakers, accurately add Mn standard solution (50µg Mn/mL) in incrementally increasing volumes from 0 - 20.0mL (0-1.0mg of Mn), and bring to volume with water.

If the Mn content in the sample is greater than 0.2%, prepare several 300mL beakers, and transfer to each of these the same amount of Ni and Fe as those contained in the sample. Perform the same procedure as that described in sample pretreatment f) Co, Cu, Mn, and after preparing an aliquot according to procedure (1), accurately add to these beakers Mn standard solution (50µg Mn/mL) in incrementally increasing volumes from 0 - 10.0mL (0-0.5mg of Mn), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 279.5nm |
| Calibration curve concentration range | 0.5 - 10µg/mL (for ≤0.2% Mn) |
| | 0.2 - 5µg/mL (for ≥0.2% Mn) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 23) |

Note:

If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### **I** Si

Reagents

(1) Si standard solution (1000µg Si/mL) : Measure out 0.5349g of silicon dioxide (purity ≥99.9%), and transfer to a 100mL polyethylene beaker. Cover the beaker, add 15mL of nitric acid (1+2) and 7mL of hydrofluoric acid, and set aside at ambient temperature for 1 hour to allow decomposition. Next, transfer this solution to a 250mL polyethylene volumetric flask, and bring to volume with water.

(2) Nb solution (10mg Nb/mL) : Same as Al VI, Reagent (2)

(3) Fe solution (10mg Fe/mL) : Same as Al VI, Reagent (3)

Procedure

(1) (1) The solution prepared according to Sample Pretreatment e) Al, Si, Sn is measured as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 100mL polyethylene volumetric flasks, and to each of these, accurately add 13mL of Nb solution (10mg Nb/mL) and 5.5mL of Fe solution (10mg Fe/mL). Further, accurately add Si standard solution (1000μg Si/mL) in incrementally increasing volumes from 0 - 6.0mL (0-6.0mg of Si), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 251.6nm |
| Calibration curve concentration range | 6 - 60μg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 34) |

**I** Sn

Reagents

(1) Sn standard solution (1000μg Si/mL) : Measure out 0.250g of Sn (purity ≥99.9%), and transfer to a 300mL polyethylene beaker. Cover the beaker, add 10mL of hydrofluoric acid, and add 1.0mL of nitric acid to gradually decompose. Transfer this solution to a 250mL polyethylene volumetric flask, and bring to volume with water.

(2) Nb solution (10mg Nb/mL) : Same as Al VI, Reagent (2)

(3) Fe solution (10mg Fe/mL) : Same as Al VI, Reagent (3)

Procedure

(1) (1) The solution prepared according to Sample Pretreatment e) Al, Si, Sn is measured as is.

For the blank test, the solution, which is measured, should be pretreated in the same way as the standards and samples, and should contain only the reagents, with the same concentrations, as those used in the standards and samples. The blank measurement result is used to correct subsequent standard and sample measurement values.

(2) To prepare standard solutions for generating a calibration curve, prepare several 100mL polyethylene volumetric flasks, and to each of these, accurately add 13mL of Nb solution (10mg Nb/mL) and 5.5mL of Fe solution (10mg Fe/mL). Further, accurately add Sn standard solution (1000μg Si/mL) in incrementally increasing volumes from 0 - 6.0mL (0-6.0mg of Sn), and bring to volume with water.

Measurement

| | |
|---|---|
| Measurement wavelength | 224.6nm |
| Calibration curve concentration range | 6 - 60μg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 37) |

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# Atomic Absorption Analysis Cookbook

## Section 10

### Analysis of Medicines

### Analysis of Biological Substances

SHIMADZU CORPORATION
KYOTO, JAPAN

Atomic Absorption Analysis Cookbook Section 10

Table of Contents

# Introduction

Cookbook Section 10 describes the analysis methods for medicines and biological substances.

With respect to the analysis methods for medicines, the Japanese Pharmacopoeia Revision 13 specifies the elements that can be analyzed using the atomic absorption method. Using these described analysis methods as a standard, the techniques were modified in the best way for analysis using the Shimadzu Atomic Absorption Spectrophotometer.

The analysis methods for biological substances are based on the tests used by the Applications Technology Division of the Kyoto Customer Support Center. Note that since there is a great variation among the biological substances depending on the specimen composition, the described pretreatment methods, interference during measurement, background absorption, flame conditions, etc. may not be the most optimum for the application.

Because the measurement conditions are set with respect to the Shimadzu AA-6000 Series Atomic Absorption Spectrophotometer, it is necessary to modify the measurement conditions when using another type of atomic absorption spectrophotometer so that the calibration curve concentration ranges match.

# 18 Analysis of Medicines

## 18.1 Purity Testing

Reference Materials

Japanese Pharmacopoeia Revision 13, Japanese Pharmacopoeia Commentary Editorial Committee, Hirokawa Book Store

### 18.1.1 Furnace Atomic Absorption Method

a) Target Elements
Pb

b) Sample Pretreatment and Measurement Procedure

- Pb (matrix: refined white sugar)

Reagents

1) Pb standard solution (0.02µg Pb/mL): Refer to Cookbook Section 2, Section 3 Preparing Standards
2) Palladium (II) nitrate solution (100µg Pd/mL): Add 15mL of nitric acid (1+1) to 0.108g of palladium (II) nitrate, heat to dissolve, and bring volume to 500mL using water.
3) Nitric acid: For measurement of toxic metals

Pretreatment

Accurately weigh out 0.050g of sample, transfer to a poly tetrafluoroethylene decomposition container, add 0.5mL of nitric acid to dissolve, seal with a cap, and heat at 150°C for 5 hours. After cooling, accurately add enough water to bring the total volume to 5.0mL. This will be used as the sample solution.

Procedure

Transfer precisely 1.0mL of the pretreated sample solution to each of four 2mL micro volumetric flasks. Accurately add the Pb standard solution (0.02µg Pb/mL) in incrementally increasing volumes from 0.1 - 0.6mL to three of the four flasks, leaving the fourth flask empty. Then add 0.2mL of palladium (II) nitrate solution (100µg Pd/mL) to each of the four flasks, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Calibration curve concentration range | 2 - 15µg/mL (Standard Addition Method) |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |
| Tube | High-density graphite tube |
| Sample injection volume | 20µL |
| Heating conditions | |

|  | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 10 | S | 0.0H |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2000 | 3 | S | 0.0 |
| 7 | 2500 | 2 | S | 1.0 |

Assessment: ≤ Pb 0.5ppm

### 18.1..2 Flame Atomic Absorption Method

a) Target Elements
Cd, Cu, Na, Pb, Zn

b) Sample Pretreatment and Measurement Procedure

- Cd (matrix: ordinary water)
  Reagents

1) Cd standard solution (1μg Cd/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Ammonium citrate solution (250g/L): Dissolve 25.0g of citric acid in water, and bring volume to 100.0mL using water.
3) Bromthymol blue solution (0.1w/v%): Dissolve 0.1g of Thymol Blue in ethyl alcohol (95%). Bring total volume of solution to 100.0mL with ethyl alcohol.
4) Ammonium sulfate solution (400g/L): Dissolve 40.0g of ammonium sulfate in water, and bring volume to 100.0mL with water.
5) Diethyldithiocarbamic acid sodium salt solution (5w/v%): Dissolve 5.0g of diethyldithiocarbamic acid sodium salt in water, and bring total volume to 100.0mL.
6) 4-methyl-2-pentanone (MIBK)
7) Nitric acid, aqueous ammonia

Procedure

1) Transfer 50.0mL of the sample solution to a 100mL separatory funnel. Add 0.5mL of nitric acid, shake well to mix the solutions, and set aside for 1 hour. To this solution, add 10.0mL of ammonium citrate solution (250g/L) and 2 drops of bromthymol blue solution (0.1w/v%). Add aqueous ammonia until the yellow color of the liquid turns green. To this solution, add 10.0mL of ammonium sulfate solution (400g/L) and 5.0mL of diethyldithiocarbamic acid sodium salt solution (5w/v%) and mix. After setting aside for several minutes, add 10.0mL of MIBK and shake

vigorously to mix. Set aside, and then collect the MIBK phase, using this as the sample solution.

2) For the standard solution, take 0.5mL of Cd standard solution (1µg Cd/mL) and dilute this to 50.0mL with water. Then transfer to a 100mL separatory funnel. The rest of the preparation procedure for the standard solution is the same as that performed for the sample.

Measurement

| | |
|---|---|
| Measurement wavelength | 228.8nm |
| Standard concentration | 0.05µg/mL (concentration after extraction) |
| Measurement conditions | |
| Lamp current | 8mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |
| Burner height | 7mm |
| Support gas | Air |
| Fuel gas flow rate | C2H2 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

Assessment: Absorbency of sample solution at measurement is to be less than that of standard solution (≤ 0.01mg/L)

### l Cu (matrix: ordinary water)

Reagent

1) Cu standard solution (10µg Cu/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Nitric acid

Procedure

1) Add 0.5mL of nitric acid to 50.0mL of sample, shake solution to mix, and set aside for 1 hour. This is used as the sample solution.
2) For the standard solution, take 5.0mL of Cu standard solution (10µg Cu/mL), accurately add water to bring solution volume to 50.0mL, then add 0.5mL of nitric acid.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.7nm |
| Standard solution concentration | 1µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 15) |

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤

1mg/L)

- Na (matrix: calcium polystyrene sulfonate)

Reagents

Na standard solution (50µg Fe/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Pretreatment Procedure

Precisely weigh 1.0g of dried sample into a 50mL beaker, and add 5.0mL of hydrochloric acid (3 mol/L) to disperse the sample. Prepare a 50mL volumetric flask to serve as a receptacle, and above this, a 12mm i.d. chromatographic column that is 70mm in length. The base of the column should be filled with glass wool. Filter the sample solution through the apparatus, and thoroughly wash with a small amount of hydrochloric acid (3mol/L). Further, continue the extraction using hydrochloric acid until the solution volume is about 45mL. Add water to bring the solution to volume (50mL).

Procedure

1) Precisely measure out a 2.0mL aliquot of the pretreated sample, and accurately add hydrochloric acid (0.02 mol/L) to bring the total volume to 500mL. This is used as the sample solution.
2) For the standard solutions, accurately add Na standard solution (50µg Na/mL) in incrementally increasing volumes from 1.0 – 6.0mL to several 100mL volumetric flasks, then bring up to volume with hydrochloric acid (0.02 mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 589.0nm |
| Calibration curve concentration range | 0.5 - 3µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 24) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

Assessment: ≤Na 1%

- Pb I (matrix: titanium oxide)

Reagents

1) Pb standard solution (10µg Pb/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Ammonium citrate solution (450g/L): Dissolve 45.0g of citric acid in water, and bring volume to 100.0mL using water.

3) Ammonium sulfate solution (400g/L)
4) Thymol Blue solution (0.1w/v%)
5) Dithizone + n-butyl acetate solution (2g/L): Add 1.0g of dithizone (1.5-diphenylthiocarbazone) to 500mL of n-butyl acetate solution, mix well to dissolve, then filter using type 5A filter paper.
6) Ammonia solution (10%): Dilute 10.0mL of aqueous ammonia to a volume of 100.0mL.
7) Potassium hydrogen sulfate: Reagent grade

Reagents 3) and 4) are prepared in the same way as reagents 2) and 3) used for Cd analysis

Pretreatment procedure

Weigh 1.0g of sample into a platinum crucible, then add 10.0g of potassium hydrogen sulfate. Heat gently at first, then while occasionally shaking, heat strongly until the liquid contents becomes transparent. After cooling, add 20.0mL of ammonium citrate solution (450g/L) and 50.0mL of water, and heat over a water bath to dissolve. After cooling, add water to bring solution volume to 100.0mL. Use this as the sample source solution.

Procedure

1) Transfer 25.0mL of the sample source solution to a 100mL separatory funnel. Add 10.0mL of ammonium sulfate solution (400g/L) and 5 drops of thymol blue solution (0.1w/v%), then accurately add 20.0mL of Dithizone + n-butyl acetate solution (2g/L). Shake for 10 minutes to mix. Set aside, and collect the n-butyl acetate phase to use for analysis.
2) For the standard solution, transfer 6.0mL of Pb standard solution (10μg Pb/mL) to a platinum crucible. The rest of the procedure is the same as that described for the sample.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Standard concentration | 3μg/mL (concentration after extraction) |
| Measurement conditions | |
| Lamp current | 10mA |
| Slit width | 0.5nm |
| Lamp mode | BGD2 |
| Burner height | 7mm |
| Support gas | Air |
| Fuel gas flow rate | C2H2 0.8L/min (If the flame appears red when spraying sample, decrease the amount of sample being suctioned.) |

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤ 0.24mg/L)

- Pb II (matrix: ordinary water)

Reagents

1) Pb standard solution (10μg Pb/mL): Same as for Pb I reagent
2) Ammonium citrate solution (250g/L)
3) Bromthymol blue solution (0.1w/v%)
4) Ammonium sulfate solution (400g/L)
5) Diethyldithiocarbamic acid sodium salt solution (5w/v%)
6) 4-methyl-2-pentanone (MIBK)
7) Nitric acid, aqueous ammonia

Note: Reagents 2) - 7) are the same as reagents 2) - 7) for the Cd analysis

Procedure

1) Transfer 50.0mL of the sample solution to a 100mL separatory funnel. Add 0.5mL of nitric acid, shake well to mix the solutions, and set aside for 1 hour. The rest of the preparation procedure for the sample solution is the same as that described in Cd Procedure 1).
2) For the standard solution, take 0.5mL of Pb standard solution (10μg Pb/mL) and dilute this to 50.0mL with water. Transfer to a 100mL separatory funnel. The rest of the preparation procedure for the standard solution is the same as that performed for the sample.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Standard concentration | 0.05μg/mL (concentration after extraction) |
| Measurement conditions | Same as for Pb I |

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤ 1mg/L)

### 18.1.3 Reduction Vaporization Atomic Absorption Method

a) Target Elements

Hg

b) Sample Pretreatment and Measurement Procedure

- Hg I (matrix: hydrochloric acid, dilute hydrochloric acid)

Reagents

1) Hg standard solution (0.1μg Hg/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Stannous chloride solution (10w/v%): Add 60.0mL of sulfuric acid (1 part sulfuric acid, 20 parts water mixture) to 10.0g of tin (II) chloride dihydrate. Mix while heating to dissolve. After cooling,

dilute with water to a volume of 100.0mL.

Procedure

1) For hydrochloric acid samples, accurately add water to 20.0mL of sample to bring the volume to 100.0mL. Use this as the sample solution.
   For dilute hydrochloric acid samples, accurately add water to 80.0mL of sample to bring the volume to 100.0mL. Use this as the sample solution.
2) For the standard solution, use water to dilute 8.0mL of Hg standard solution (0.1µg Hg/mL) to 100.0mL.

Measurement

Connect the MVU-1A Mercury Vaporization Unit to the atomic absorption spectrophotometer, and measure the sample solution and the standard solution. Refer to the MVU-1A instruction manual for operation instructions.

| | |
|---|---|
| Measurement wavelength | 253.7nm |
| Standard concentration | 8ng/mL |
| Measurement conditions | |
| Lamp current | 4mA |
| Slit width | 0.5nm |
| Lamp mode | BGC-D2 |

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (For hydrochloric acid, ≤0.04ppm; for dilute hydrochloric acid, ≤0.01ppm).

Hg II (matrix: sodium hydroxide)

Reagents

1) Hg standard solution (0.1µg Hg/mL)
2) Stannous chloride solution (10w/v%)
3) Potassium permanganate solution (60g/L): Dissolve 6.0g of potassium permanganate in water, and dilute with water to 100.0mL.
4) Hydroxylamine hydrochloride solution (200g/L): Dissolve 20.0g of hydroxylamine hydrochloride in water, and dilute with water to 100.0mL.

Note: Reagents 1) and 2) are the same as reagents 1) and 2) for the Hg I analysis.

Pretreatment Procedure

1) Dissolve 2.0g of sample and 1.0mL of potassium permanganate solution (60g/L) in 30.0mL of water. Gradually add hydrochloric acid (containing no Hg) to neutralize the solution, then add 5.0mL of sulfuric acid (1+1). After adding enough hydroxylamine hydrochloride solution (200g/L)

to dissolve the manganese dioxide precipitate, accurately add water to bring the total volume to 100.0mL. Use this as the sample solution.

Procedure

1) The pretreated sample solution is measured just as it is.
2) For the standard solution, add 1.0mL of potassium permanganate solution (60g/L) to 2.0mL of Hg standard solution (0.1µg Hg/mL), and the same amounts of hydrochloric acid and hydroxylamine hydrochloride solution (200g/L) used to prepare the sample solution. Accurately add water to bring the total volume to 100.0mL.

Measurement

Same as that for Hg I (Using standard solution concentration of 2ng/mL)

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (For hydrochloric acid, ≤0.04ppm; for dilute hydrochloric acid, ≤0.1ppm).

Hg III (matrix: gelatin, refined gelatin)

Reagents

Same as reagents 1) - 4) for the Hg II analysis.

Pretreatment Procedure

1) Weigh 2.0g of sample into a decomposition flask. Add 20.0mL of sulfuric acid (1+1) and 100.0mL of potassium permanganate solution (60g/L). Connect a circulating current cooling system, heat gently, and boil for 2 hours. If the solution becomes clear during this time, decrease the temperature to about 60°C, and add another 5.0mL of potassium permanganate solution (60g/L). Boil again, and repeat this procedure until the manganese dioxide precipitate persists for about 20 minutes. After cooling, add hydroxylamine hydrochloride solution (200g/L) until the manganese dioxide precipitate disappears, and then accurately add water to bring the volume to 150.0mL. Use this as the sample solution.

Procedure

1) The pretreated sample solution is measured just as it is.
2) For the standard solution, transfer 2.0mL of Hg standard solution (0.1µg Hg/mL) to a decomposition flask. Add 20.0mL of sulfuric acid (1+1) and 100.0mL of potassium permanganate solution (60g/L) and perform the same procedure as that used to prepare the sample solution. Use this as the standard solution.

Measurement

Same as that for Hg I (Using standard solution concentration of 1.33ng/mL)

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (For hydrochloric acid, ≤0.04ppm; for dilute hydrochloric acid, ≤0.1ppm).

## 18.2 Quantitation

Reference Materials

Japanese Pharmacopoeia Revision 13, Japanese Pharmacopoeia Commentary Editorial Committee, Hirokawa Book Store

### 18.2.1 Flame Atomic Absorption Method

a) Target Elements
Ag, Al, Au, Bi, K, Na, Zn

b) Sample Pretreatment and Measurement Procedure

- Ag (matrix: sulfadiazine silver)

Reagents

Ag standard solution (50µg Ag/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Weigh out approximately 0.05g of dried sample. Dissolve in 2.0mL of nitric acid, and accurately dilute with water to a volume of 100.0mL.

Procedure

1) Transfer 1.0mL of the pretreated sample solution to a 100mL volumetric flask, add 2.0mL of nitric acid and bring up to volume with water. Use this as the sample solution.
2) For the standard solutions, accurately transfer Ag standard solution (50µg Ag/mL) to several 100mL volumetric flasks in incrementally increasing volumes from 1.0 - 6.0mL. Add 2.0mL of nitric acid to each, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 328.1nm |
| Calibration curve concentration range | 0.5 - 3µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 1) |

Assessment: Ag content 28.7 - 30.8%

- Al (matrix: Aldioxa)

Reagents

Al standard solution (200µg Al/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Weigh out precisely 0.2g of sample, add 50.0mL of hydrochloric acid (1+4), and carefully heat to dissolve. After cooling, accurately add hydrochloric acid (1+4) to a volume of 100.0mL.

Procedure

1) Transfer 5.0mL of the pretreated sample solution to a 50mL volumetric flask, and bring up to volume with water. Use this as the sample solution.
2) For the standard solutions, accurately transfer Al standard solution (200µg Al/mL) to several 100mL volumetric flasks in incrementally increasing volumes from 2.0 - 10.0mL. Add 1.0mL of hydrochloric acid to each, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 10 - 40µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 2) |

Assessment: Al content 11.1 - 13.0%

- Au (matrix: sodium aurothiomalate)

Reagents

Au standard solution (50µg Au/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Accurately weigh out 0.7g of sample. Add 10.0mL of water and 20.0mL of nitric acid (1+1). Shake well and bring volume to 100.0mL. Filter and discard the first 20.0mL of filtrate. Carefully collect the next 10.0mL of filtrate, and bring to a volume of precisely 100.0mL using water.

Procedure

1) Transfer 2.0mL of the pretreated sample solution to a 50mL volumetric flask, and bring up to volume with water. Use this as the sample solution.
2) For the standard solutions, accurately transfer Au standard solution (50µg Al/mL) to several 50mL volumetric flasks in incrementally increasing volumes from 2.0 - 10.0mL. Bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 242.8nm |
| Calibration curve concentration range | 2 - 10µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 4) |

Assessment: Au content 49.0 - 52.5%

l Bi (matrix: phellodendron, albumin tannate and bismuth subnitrate powder)

Reagents

Bi standard solution (100µg Bi/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Weigh out exactly 0.7g of sample. Add 10.0mL of water and 20.0mL of nitric acid (1+2). Shake well and add water to a volume of 100.0mL. Filter and discard the first 20.0mL of filtrate. Carefully collect the next 10.0mL of filtrate, and bring to a volume of precisely 100.0mL with water.

Procedure

1) Transfer 10.0mL of the pretreated sample solution to a 100mL volumetric flask. Bring up to volume with nitric acid (1+100). Use this as the sample solution.
2) For the standard solutions, accurately transfer Bi standard solution (100µg Bi/mL) to several 100mL volumetric flasks in incrementally increasing volumes from 5.0 - 15.0mL. Bring up to volume with nitric acid (1+100). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 223.1nm |
| Calibration curve concentration range | 5 - 15µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 8) |

Assessment: Bi content 12.9 - 16.3%

l K I (matrix: calcium polystyrene sulfonate)

Reagents

K standard solution (5mg K/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Weigh out precisely 1.0g of dried sample. Transfer to a glass container equipped with a stopper. Add 50.0mL of K standard solution (5mg K/mL), and shake for 2 hours to mix. Filter and discard the first

20.0mL of filtrate. Carefully collect the next 5.0mL of filtrate, and bring to a volume of exactly 100.0mL with hydrochloric acid (0.02mol/L).

### Procedure

1) Accurately measure out 10.0mL of the pretreated sample solution, and bring to a volume of 1000.0mL with hydrochloric acid (0.02mol/L). Use this as the sample solution.
2) For the standard solutions, dilute several aliquots of K standard solution (5mg K/mL) using hydrochloric acid (0.02mol/L), so that the range of final K concentrations is 0.5 - 2.5μg/mL. Use these solutions for measurement.

### Measurement

| | |
|---|---|
| Measurement wavelength | 766.5nm |
| Calibration curve concentration range | 0.5 - 2.5μg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 19) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

### Assessment

K replacement volume: K replacement amount in 1.0g of dried sample 0.053 - 0.071g

K replacement volume calculation

K replacement amount (mg) corresponding to 1.0g dried sample = $\frac{X-100Y}{W}$

where:

Y: K content (mg) in 1000.0mL of sample solution

X: K amount (mg) in 50.0mL of K standard solution before replacement

W: Amount of dried sample (g) used

### K II (matrix: sodium polystyrene sulfonate)

### Reagents

K standard solution (5mg K/mL): Same as for K I

### Sample Pretreatment

Accurately weigh out 1.5g of the above formula-converted dried sample, and transfer to a glass container equipped with a stopper. Add 100.0mL of K standard solution (5mg K/mL), and shake for 15 minutes to mix. Filter and discard the first 20.0mL of filtrate. Carefully collect the next 10.0mL of filtrate, and bring to a volume of 100.0mL with water.

Procedure

1) Accurately measure out 10.0mL of the pretreated sample solution, and bring to a volume of 1000.0mL with water. Use this as the sample solution.
2) For the standard solutions, dilute several aliquots of K standard solution (5mg K/mL) using water, so that the range of final K concentrations is 1 - 5µg/mL. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 766.5nm |
| Calibration curve concentration range | 1 - 5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 19) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

Assessment

K replacement volume: K replacement amount in 1.0g of the aforementioned formula-converted dried sample 0.110 - 0.135g

K replacement volume calculation

K replacement amount (mg) corresponding to 1.0g of the aforementioned formula converted dried sample = $\frac{X-100Y}{W}$

where:

Y: K content (mg) in 1000.0mL of sample solution

X: K amount (mg) in 100.0mL of K standard solution before replacement

W: Amount of converted dried sample (g) used

Na (matrix: sodium polystyrene sulfonate)

Reagents

Na standard solution (50µg Na/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Sample Pretreatment

Accurately weigh out 1.0g of the aforementioned formula-converted dried sample, and transfer to a glass container equipped with a stopper. Add exactly 50.0mL of hydrochloric acid (3mol/L) and shake for 60 minutes to mix. Filter and discard the first 20.0mL of filtrate. Carefully collect the next 5.0mL of filtrate, and bring to a volume of 100.0mL with water.

Procedure

1) Measure out 20.0mL of the pretreated sample solution, and bring to a volume of 1000.0mL with water. Use this as the sample solution.
2) For the standard solutions, prepare several 100mL volumetric flasks, and transfer Na standard solution (50µg Na/mL) to these flasks in incrementally increasing volumes from 2.0 - 6.0mL. Bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 589.0nm |
| Calibration curve concentration range | 1 - 3µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 24) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

Assessment: Na 9.4 -11.0%

**I** Zn I (matrix: isophane insulin aqueous suspension)

Reagents

Zn standard solution (10µg Zn/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) According to the displayed units, accurately measure out a volume corresponding to approximately 400 units of sample. Accurately add 1.0mL of hydrochloric acid (0.1mol/L) and 100.0mL of water. If necessary, dilute using more water so that the Zn concentration in 1.0mL is 0.6 - 1.0µg. Use this as the sample solution.
2) For the standard solutions, transfer Zn standard solution (10µg Zn/mL) to several 100mL volumetric flasks in incrementally increasing volumes from 3.0 - 12.0mL. Add 1.0mL of hydrochloric acid (0.1mol/L), and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Calibration curve concentration range | 0.3 - 1.2µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 44) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

Assessment: Zn 0.01 -0.04mg per 100 units of suspension

- Zn II (matrix: insulin)

Reagents

Zn standard solution (10µg Zn/mL): Same as for Zn I

Procedure

1) Measure out 0.01g of sample. Add precisely 1.0mL of hydrochloric acid (0.1mol/L) and 200.0mL of water. If necessary, dilute using more water so that the Zn concentration in 1mL is 0.6 - 1.0µg. Use this as the sample solution.
2) For the standard solutions, perform the same procedure as for Zn I, Procedure, 2).

Measurement: Same as for Zn I

Assessment: Zn 0.27 - 1.08%

- Zn III (matrix: insulin zinc injection aqueous suspension), crystalline insulin zinc injection aqueous suspension), amorphous insulin zinc injection aqueous suspension)

Reagents

Zn standard solution (10µg Na/mL): Same as for Zn I

Procedure

1) According to the displayed units, accurately measure out a volume corresponding to approximately 200 units of sample. Add 1.0mL of hydrochloric acid (0.1mol/L) and 200.0mL of water. If necessary, dilute using more water so that the Zn concentration in 1mL is 0.6 - 1.0µg. Use this as the sample solution.
2) For the standard solutions, perform the same procedure as for Zn I, Procedure, 2).

Measurement: Same as for Zn I

Assessment: Zn 0.12 -0.30mg per 100 units of suspension

## 18.3 Test Method for Rubber Stoppers used for Transported Liquids

Reference Materials

Japanese Pharmacopoeia Revision 13, Japanese Pharmacopoeia Commentary Editorial Committee, Hirokawa Book Store

### 18.3.1 Sample Pretreatment

a) Impurities (Cd, Pb)

Wash the rubber stopper with water, dry it at ambient temperature, and cut it into fine pieces. Mix the pieces well, and measure 2.0g of the pieces into a platinum or quartz glass crucible. Add 2mL of sulfuric acid to moisten. Heat gradually to dry, and then heat at 450 - 500°C to ash. If ashing is incomplete, moisten with 1mL of sulfuric acid, heat to dryness, and then ash. If necessary, repeat this process. After cooling, moisten the residue with water, add 2 - 4mL of hydrochloric acid, and heat on a water bath to evaporate to dryness. Add another 1 - 5mL of hydrochloric acid, and heat to dissolve. Next, add 0.5 - 1mL of 50% citric acid solution and hydrochloric acid (1+1) and 0.5 - 1mL of heated ammonium acetate solution (40%) to dissolve the sample. (If any impurities remain, filter through a glass filtration device.)

b) Extracted substance (Zn)

Wash the rubber stopper and dry at ambient temperature. Place this in hard glass container. Add water at a weight 10 times that of the sample weight, and after appropriately capping the container, place it in a high-pressure steam sterilizer and heat at 121°C for 1 hour. Remove the glass container from the sterilizer and set it aside until it cools to ambient temperature, then immediately remove the rubber stopper and use the liquid as the sample source liquid.

### 18.3.2 Flame Atomic Absorption Method

a) Target Elements

Cd, Pb, Zn

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current, slit width and flame conditions, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

- Cd

Reagents

1) Cd standard solution (1µg Cd/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Ammonium citrate solution (250g/L)
3) Bromthymol blue solution (0.1w/v%)
4) Ammonium sulfate solution (400g/L)
5) Diethyldithiocarbamic acid sodium salt solution (5w/v%)
6) 4-methyl-2-pentanone (MIBK)

Reagents 2) - 6) are the same as those described in Paragraph 18.1.2, Cd Reagents 2) - 6)

7) Aqueous ammonia (10%): Take 10.0mL of aqueous ammonia and dilute to 100.0mL with water.

Procedure

1) Transfer all of the pretreated sample solution to a 200mL separatory funnel. Add 10.0mL of ammonium citrate solution (250g/L) and 2 drops of bromthymol blue solution (0.1w/v%). Add aqueous ammonia (10%) until the yellow color of the liquid turns green. To this solution, add 10.0mL of ammonium sulfate solution (400g/L), and add water to bring the volume to 100.0mL. Next, add 20.0mL of diethyldithiocarbamic acid sodium salt solution (5w/v%) and mix. After setting aside for several minutes, add 20.0mL of MIBK and shake vigorously to mix. Set aside, and

then collect the MIBK phase, using this as the sample solution. If necessary, filter this solution.

2) For the standard solution, transfer 10.0mL of Cd standard solution (1µg Cd/mL) to a 200mL separatory funnel. Add 10.0ml of ammonium citrate solution (250g/L) and 2 drops of bromthymol blue solution (0.1w/v%). The rest of the preparation procedure for the standard solution is the same as that performed for the sample.

Measurement

| | |
|---|---|
| Measurement wavelength | 228.8nm |
| Standard concentration | 0.5µg/mL (concentration after extraction) |

Measurement conditions: Same as that described Paragraph 16.1.2 Flame Atomic Absorption Method, Cd Measurement Conditions

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤ 5ppm)

Pb

Reagents

1) Pb standard solution (10µg Pb/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Ammonium citrate solution (250g/L)
3) Bromthymol blue solution (0.1w/v%)
4) Ammonium sulfate solution (400g/L)
5) Diethyldithiocarbamic acid sodium salt solution (5w/v%)
6) 4-methyl-2-pentanone (MIBK)
   Reagents 2) - 6) are the same as those described in Paragraph 18.1.2, Cd Reagents 2) - 6)
7) Aqueous ammonia (10%): Same as for Cd Reagents, 7)

Procedure

1) Same as Cd Procedure 1)
2) For the standard solution, transfer 1.0mL of Pb standard solution (10µg Cd/mL) to a 200mL separatory funnel. Add 10.0ml of ammonium citrate solution (250g/L) and 2 drops of bromthymol blue solution (0.1w/v%). The rest of the preparation procedure for the standard solution is the same as that performed for the sample.

Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Standard concentration | 0.5µg/mL (concentration after extraction) |

Measurement conditions: Same as that described in Paragraph 16.1.2 Flame Atomic Absorption Method, Pb I Measurement Conditions

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤ 5ppm)

- Zn

Reagents

Zn standard solution (10µg Zn/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Using 10.0mL of pretreated sample, accurately add nitric acid (1+50) to a volume of 20mL. Use this as the sample solution.
   For the blank test, perform the same procedure on water as performed on the sample. Take 10.0mL of this solution, and accurately add nitric acid (1+50) to a volume of 20.0mL. The resulting measurement of the blank is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, take 1.0mL of Zn standard solution (10µg Zn/mL), and accurately add nitric acid (1+50) to a volume of 20.0mL.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Standard concentration | 0.5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 44) |

Assessment: Absorbance of sample solution at measurement is to be less than that of standard solution (≤Zn 0.25µg/mL of eluate)

# 19 Analysis of Medicines

## 19.1 Blood Serum Analysis Method

### 19.1.1 Furnace Atomic Absorption Method

a) Target Elements

Al

Reference Materials

Shimadzu Commentary Vol. 37. No1. P75 (1980)

Shimadzu Commentary Vol. 40. No4. P17 (1983)

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current and slit width, refer to Cookbook Section 4, Paragraph 7.5 Measurement Conditions According to Element.

l Al

Reagents

Al standard solution (100ng Al/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Measure 2.0mL of serum into a 10mL volumetric flask, and bring up to volume with water. Use this solution for measurement.
2) For the standard solutions, accurately add Al standard solution (100ng Al/mL) in incrementally increasing volumes from 0.2 - 2.0mL to several 10mL volumetric flasks, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 309.3nm |
| Calibration curve concentration range | 2 - 20ng/mL |
| Tube | pyrolyzed graphite tube |
| Sample injection volume | 20µL |

Heating conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 800 | 10 | R | 1.0 |
| 4 | 800 | 20 | S | 1.0 |
| 5 | 800 | 3 | S | 0.0H |
| 6 | 2500 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

### 19.1.2 Flame Atomic Absorption Method

a) Target Elements
Ca, Cu, Fe, K, Mg, Na

Reference Materials

Shimadzu Commentary Vol. 37. No1. P75 (1980)

b) Sample Pretreatment

- Ca, K, Mg, Na

  Dilute the serum so that the concentration is within the calibration curve concentration range. Use the solution for measurement. For analysis of Ca and Mg, add La to inhibit interference.

- Cu, Fe

  Transfer 2.0mL of serum to a centrifuge separation tube. Add 2.0mL of hydrochloric acid (1+1) and 2.0mL of trichloroacetic acid solution (200g/L) and mix well. Set aside for 5 minutes, and then centrifuge at 3000rpm for 5 minutes. Transfer the upper layer supernatant to a test tube using a pipette, and use this solution for measurement.

c) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current, slit width and flame conditions, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

- Ca

Reagents

1) Ca standard solution (10μg Ca/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) La solution (50g La/L): Weigh out 67.0g of lanthanum oxide (heptahydrate) and gradually add hydrochloric acid (1+1) to dissolve. Add water to bring the volume to 500.0mL.

Procedure

1) Measure 1.0mL of serum into a 50mL volumetric flask, add 3.0mL of La solution (50g La/L), and bring to volume with water. Use this solution for measurement.
   For the blank test, measure 3.0mL of La solution (50g La/L) into a 50mL volumetric flask, and bring up to volume with water. After measuring this solution, the result is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, accurately add Ca standard solution (10μg Ca/mL) in incrementally increasing volumes from 5.0 - 25.0mL to several 50mL volumetric flasks. Add 3.0mL of La solution (50g La/L) to each, and bring to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 422.7nm |
| Calibration curve concentration range | 1 - 5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 9) |

- Cu

Reagents

1) Cu standard solution (10µg Cu/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) The pretreated sample solution is used as is for measurement.
   For the blank test, measure 2.0mL of water into centrifuge separation tube, and perform the same procedure as that performed on the sample solution. After measuring this solution, the result is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, accurately add Cu standard solution (10µg Cu/mL) in incrementally increasing volumes from 1.0 - 5.0mL to several 50mL volumetric flasks. Add 10.0mL of hydrochloric acid (1+1) to each, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.8nm |
| Calibration curve concentration range | 0.2 - 1µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 15) |

- Fe

Reagents

1) Fe standard solution (10µg Fe/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Same as that for Cu 1).
2) For the standard solutions, accurately add Fe standard solution (10µg Fe/mL) in incrementally increasing volumes from 2.0 - 10.0mL to several 50mL volumetric flasks. Add 10.0mL of hydrochloric acid (1+1) to each, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |

| | |
|---|---|
| Calibration curve concentration range | 0.4 - 2µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 16) |

### K

Reagents

1) K standard solution (10µg K/mL)
2) Na standard solution (100µg Na/mL)

For 1) and 2) Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Measure 5.0mL of serum into a 100mL volumetric flask, and bring to volume with water. Transfer a 4.0mL aliquot of this solution to another 100mL flask and bring to volume with water. Use this solution for measurement.
2) For the standard solutions, accurately add K standard solution (10µg K/mL) in incrementally increasing volumes from 1.0 - 8.0mL to several 100mL volumetric flasks. Add to each of these 6.0mL of Na standard solution (100µg Na/mL), then bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 766.5nm |
| Calibration curve concentration range | 0.1 - 0.8µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 19) |

### Mg

Reagents

1) Mg standard solution (5µg Mg/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) La solution (50g La/L): Same as for Ca Reagents, 2)

Procedure

1) Measure 0.5mL of serum into a 50mL volumetric flask. Add 3.0mL of La solution (50g La/L) and bring to volume with water. Use this solution for measurement.
   For the blank test, measure 3.0mL of La solution (50g La/L) into a 50mL volumetric flask, then bring up to volume with water. After measuring this solution, the result is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, accurately add Mg standard solution (5µg Mg/mL) in incrementally increasing volumes from 1.0 - 5.0mL to several 50mL volumetric flasks. Add 3.0mL of La solution (50g La/L) to each, then bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 285.2nm |
| Calibration curve concentration range | 0.1 - 0.5µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 21) |

- Na

Reagents

1) Na standard solution (10µg Na/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Measure 1.0mL of serum into a 100mL volumetric flask, and bring to volume with water. Transfer a 2.0mL aliquot of this solution to another 100mL flask and bring to volume with water. Use this solution for measurement.
2) For the standard solutions, accurately add Na standard solution (10µg Na/mL) in incrementally increasing volumes from 1.0 - 8.0mL to several 100mL volumetric flasks, and bring up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 589.0nm |
| Calibration curve concentration range | 0.1 - 0.8µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 24) |

Note: If the absorbance of the standard solution exceeds 0.5, adjust the burner angle so that the absorbance of the standard solution having the highest concentration is about 0.5.

## 19.2 Whole Blood Analysis Method

### 19.2.1 Furnace Atomic Absorption Method

a) Target Elements

Pb

Reference Materials

Shimadzu Commentary Vol. 40. No4. P11 (1983)

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current and slit width, refer to Cookbook Section 4, Paragraph 7.5 Measurement Conditions According to Element.

## l Pb

### Reagents

1) Pb standard solution (50ng Pb/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards
2) Triton X solution (10w/v%): Dissolve 10.0g of Triton X-100 in water, and dilute with water to a volume of 100.0mL.
3) Ammonium phosphate solution (10w/v%): Dissolve 10.0g of triammonium phosphate trihydrate, and dilute with water to a volume of 100.0mL.

### Procedure

1) Measure 0.5mL of serum into a 10mL volumetric flask. Add 1.0mL of Triton X solution (10w/v%) and 2.5mL of ammonium phosphate solution (10w/v%), then bring up to volume with water. Use this solution for measurement.
2) For the standard solutions, accurately add Pb standard solution (50µg Pb/mL) in incrementally increasing volumes from 0.4 - 2.0mL to several 10mL volumetric flasks. Add 1.0mL of Triton X solution (10w/v%) and 2.5mL of ammonium phosphate solution (10w/v%) to each of these, then bring up to volume with water. Use these solutions for measurement.

### Measurement

| | |
|---|---|
| Measurement wavelength | 283.3nm |
| Calibration curve concentration range | 2 - 10ng/mL |
| Tube | High-density graphite tube |
| Sample injection volume | 20µL |

Heating conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 400 | 10 | R | 1.0 |
| 4 | 400 | 20 | S | 1.0 |
| 5 | 400 | 3 | S | 0.0H |
| 6 | 1800 | 3 | S | 0.0H |
| 7 | 2500 | 2 | S | 1.0 |

## 19.3 Urine Analysis Method

### 19.3.1 Furnace Atomic Absorption Method

a) Target Elements
Cr

Reference Materials

Shimadzu Commentary Vol. 41. No4. P61 (1984)

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current and slit width, refer to Cookbook Section 4, Paragraph 7.5 Measurement Conditions According to Element.

- Cr

Reagents

1) Cr standard solution (25ng Cr/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

Transfer 10.0mL aliquots of urine to each of four 25mL volumetric flasks. Do not add any Cr standard solution (25ng Cr/mL) to one of these flasks. Accurately add the Cr standard solution in incrementally increasing volumes from 1.0 - 5.0mL to the remaining three flasks, and then bring each of these up to volume with water. Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 357.9nm |
| Calibration curve concentration range | 1 - 5ng/mL |
| Tube | Pyrolyzed graphite tube |
| Sample injection volume | 20µL |

Heating conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 700 | 10 | R | 1.0 |
| 4 | 700 | 20 | S | 1.0 |
| 5 | 700 | 3 | S | 0.0H |
| 6 | 2500 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

## 19.4 Tissue Analysis Method

### 19.4.1 Sample Pretreatment

a) Decomposition with nitric acid and perchloric acid

Weigh out 2 - 5g of the collected tissue specimen, and transfer to a 200mL conical beaker. Add 20.0mL of nitric acid (1+1), and heat gently to initiate a reaction with the sample. After cooling, add 2.0mL of perchloric acid, and heat gently to concentrate. When the contents begins to turn a dark color, add nitric acid, 2 -3 mL at a time, and continue heating. When the contents begin to appear slightly yellowish or colorless, continue heating until the white fumes of perchloric acid are generated. Cool, and then add 5.0mL of nitric acid (1+1) and heat to dissolve the salts. After cooling again, dilute with water to the same volume. Use this solution for measurement.

**CAUTION:**

1) If during the decomposition process the sample becomes carbonized or dried, it will explode. For this reason, be sure that nitric acid has been added before heating.
2) If the contents should become carbonized, the target element may be lost due to volatilization.
3) Since there is a possibility of contamination due to impurities in the reagents or lab ware, a blank solution is prepared using reagent only, and is processed in the same way as the sample.

b) Dry Ashing

Weigh out 2 - 10g of sample that has been air-dried, and transfer to a 100mL quartz glass beaker. Heat gently on a hot plate. Continue heating until sufficient water has been eliminated to the point of partial carbonization. Transfer to an electric furnace, and heat so that the temperature rises at about 100°C per hour. Then heat at 500°C for several hours up to 10 hours, until ashing is completed. Add 2 - 4mL of water to the ash, and dry over a water bath. Add 5.0mL of nitric acid (1+1) to dissolve the salts, and dilute with water to a fixed volume. Use this solution for measurement.

Note: There is a possibility of volatilization of nearly all elements. Cd will be volatilized at an ashing temperature above 500°C. If halogens are present, As, Sb, Sn and Zn, etc. are easily volatilized. Heating above 550°C will cause a substantial reduction in element recovery.

### 19.4.2 Furnace Atomic Absorption Method

a) Target Elements

Cu, Mn

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current and slit width, refer to Cookbook Section 4, Paragraph 7.5 Measurement Conditions According to Element.

- Cu

Reagents

1) Cu standard solution (25ng Cu/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) The pretreated sample solution is used as is for analysis. If necessary, dilute it with nitric acid (0.1mol/L) so that the target element concentration is within the calibration curve concentration range.
   For the blank test, prepare a blank test solution using the same procedure as that for the sample. The resulting measurement of the blank solution is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, accurately add Cu standard solution (25ng Cu/mL) in incrementally increasing volumes from 1.0 - 6.0mL to several 25mL volumetric flasks, then bring up to volume with nitric acid (0.1mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 324.8nm |
| Calibration curve concentration range | 1 - 6ng/mL |
| Tube | Pyrolyzed graphite tube |
| Sample injection volume | 10µL |
| Heating conditions | |

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 500 | 10 | R | 1.0 |
| 4 | 500 | 15 | S | 1.0 |
| 5 | 500 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

- Mn

Reagents

1) Mn standard solution (25ng Mn/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) The pretreated sample solution is used as is for analysis. If necessary, dilute it with nitric acid (0.1mol/L) so that the target element concentration is within the calibration curve concentration range.
   For the blank test, prepare a blank test solution using the same procedure as that for the sample. The resulting measurement of the blank solution is used to correct subsequent standard and sample measurement values.

2) For the standard solutions, accurately add Mn standard solution (25ng Mn/mL) in incrementally increasing volumes from 0.5- 3.0mL to several 25mL volumetric flasks, then bring up to volume with nitric acid (0.1mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 279.5nm |
| Calibration curve concentration range | 0.5 - 3ng/mL |
| Tube | Pyrolyzed graphite tube |
| Sample injection volume | 10μL |

Heating conditions

| | TEMP (°C) | TIME (sec) | HEAT | GAS (L/min) |
|---|---|---|---|---|
| STAGE 1 | 120 | 15 | R | 0.1 |
| 2 | 250 | 10 | R | 0.1 |
| 3 | 600 | 10 | R | 1.0 |
| 4 | 600 | 15 | S | 1.0 |
| 5 | 600 | 3 | S | 0.0H |
| 6 | 2300 | 3 | S | 0.0H |
| 7 | 2700 | 2 | S | 1.0 |

### 19.4.3 Flame Atomic Absorption Method

a) Target Elements

Cd, Fe, Zn

b) Measurement Procedure

Measurement is conducted using the following procedures. For lamp current, slit width and flame conditions, refer to Cookbook Section 3, Paragraph 6.4 Measurement Conditions According to Element.

- Cd

Reagents

1) Cd standard solution (10µg Cd/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) The pretreated sample solution is used as is for analysis. If necessary, dilute it with nitric acid (0.1mol/L) so that the target element concentration is within the calibration curve concentration range.
   For the blank test, prepare a blank test solution using the same procedure as that for the sample. The resulting measurement of the blank solution is used to correct subsequent standard and sample measurement values.
2) For the standard solutions, accurately add Cd standard solution (10ng Cd/mL) in incrementally increasing volumes from 1.0- 6.0mL to several 100mL volumetric flasks, then bring up to volume with nitric acid (0.1mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 228.8nm |
| Calibration curve concentration range | 0.1 - 0.6µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 11) |

- Fe

Reagents

1) Fe standard solution (50µg Fe/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Same as for Cd, 1)
2) For the standard solutions, accurately add Fe standard solution (50ng Fe/mL) in incrementally increasing volumes from 1.0- 8.0mL to several 100mL volumetric flasks, then bring up to volume with nitric acid (0.1mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 248.3nm |
| Calibration curve concentration range | 0.5 - 4.0µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 16) |

Zn

Reagents

1) Zn standard solution (10µg Zn/mL): Refer to Cookbook Section 2, Paragraph 3 Preparing Standards

Procedure

1) Same as for Cd, 1)
2) For the standard solutions, accurately add Zn standard solution (10ng Zn/mL) in incrementally increasing volumes from 1.0- 6.0mL to several 100mL volumetric flasks, then bring up to volume with nitric acid (0.1mol/L). Use these solutions for measurement.

Measurement

| | |
|---|---|
| Measurement wavelength | 213.9nm |
| Calibration curve concentration range | 0.1 - 0.6µg/mL |
| Measurement conditions | Refer to Cookbook Section 3, Paragraph 6.4, 44) |