

ATOMIC ABSORPTION SPECTROPHOTOMETRY COOKBOOK

Section 2

Standard Sample Preparation Method

Prparation of Calibration Curve and Determination Method

Interference in Atomic Absorption Spectrophotometry

SHIMADZU CORPORATION

Atomic Absorption Spectrophotometry Cookbook

Section 2

CONTENTS

3. Standard Sample	1
3.1 Stock standard	1
3.2 Standard solution for calibration curve	1
3.3 Standard solution preparation method	2
4. Preparation of Calibration Curve and Determination Method	10
4.1 Calibration curve method	10
4.2 Standard addition method	11
4.3 Concentration of calibration curve	12
5. Interference in Atomic Absorption Spectrophotometry	16
5.1 Spectrophotometric interference and its correction method	16
5.2 Physical interference	20
5.3 Chemical interference and its correction method	21

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/ml.

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 electrothermal(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.

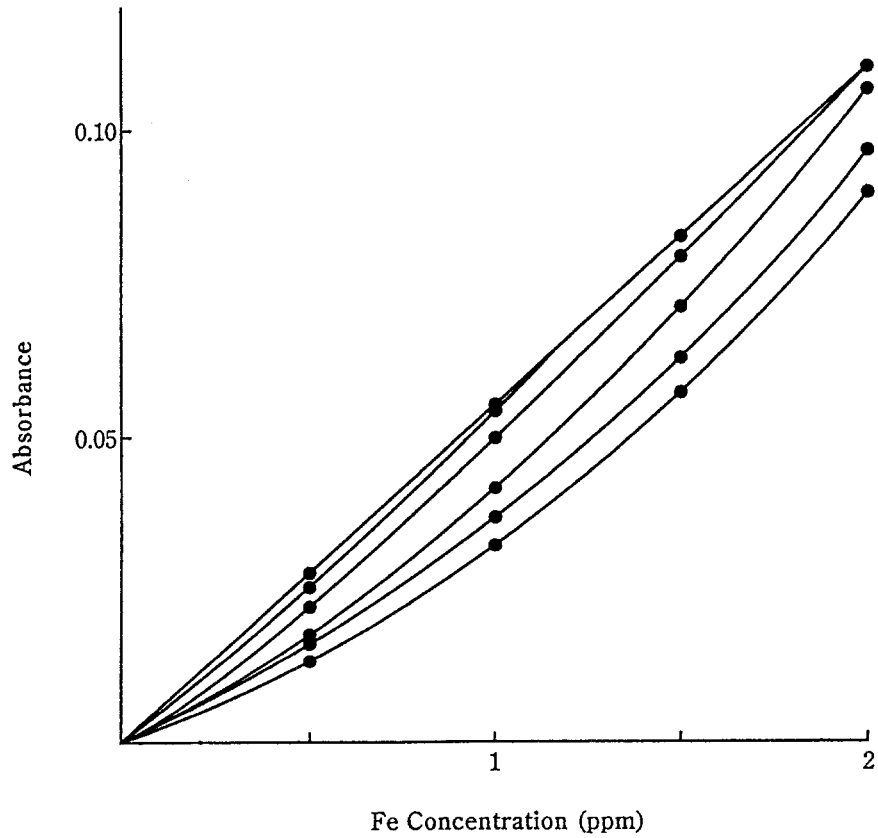


Fig. 3.1 Change on standing of Fe standard sample

3.3 Standard solution preparation method

1. Ag (Silver)

1.0mg Ag/ml Standard material : Silver nitrate (AgNO_3)

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

2. Al (Aluminum)

1.0mg Al/ml Standard material : Metal aluminum 99.9% up

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

3. As (Arsenic)
1.0mg As/ml Standard material : Arsenic (III) trioxide 99.9% up
Preparation : Arsenic (III) trioxide is heated at 105°C for about two hours and is
method of cooled with the desiccator. Its 1.320g is dissolved in the smallest
solution possible sodium hydroxide solution (1N) and is diluted with water to
1000ml accurately.
4. Au (Gold)
1.0mg Au/ml Standard material : Gold
Preparation : 0.100g of high purity gold is dissolved in several ml of aqua regia and
method of vaporized to dryness on water bath. Then, 1ml of hydrochloric acid is
solution added and vaporized to dryness. It is dissolved in hydrochloric acid and
water and diluted with water to 100ml accurately. Hydrochloric acid
concentration is set at 1N.
5. B (Boron)
1.0mg B/ml Standard material : Boric acid (H₃BO₃)
Preparation : 5.715g of pure boric acid is dissolved in water and is diluted to
method of 1000ml.
solution
6. Be (Beryllium)
1.0mg Be/ml Standard material : Metal beryllium 99.9% up
Preparation : 0.100g of metal beryllium is heated and dissolved with hydrochloric
method of acid (1+1) 10ml and is diluted with water to 100ml after it has cooled.
solution Hydrochloric acid concentration is set at 1N.
7. Bi (Bismuth)
1.0mg Bi/ml Standard material : Metal bismuth 99.9% up
Preparation : 0.100g of metal bismuth is heated and dissolved with nitric acid (1+1)
method of 20ml and is diluted to 100ml accurately after it has cooled.
solution

8. Ca (Calcium)
1.0mg Ca/ml Standard material : Calcium carbonate (CaCO_3)
Preparation : 0.2497g of calcium carbonate dried at 110°C for about one hour is
method of dissolved with hydrochloric acid (1+1) 5ml and is diluted with water to
solution 100ml accurately.
9. Cd (Cadmium)
1.0mg Cd/ml Standard material : Metal cadmium 99.9% up
Preparation : 1,000g of metal cadmium is heated and dissolved with nitric acid (1+1)
method of 30 ml and is diluted with water to 1000ml accurately after it has
solution cooled.
10. Co (Cobalt)
1.0mg Co/ml Standard material : Metal cobalt 9.9% up
Preparation : 1.000g of metal cobalt is heated and dissolved with nitric acid (1+1) 30
method of m and is diluted with water to 1000ml accurately after it has cooled.
solution
11. Cr (Chromium)
1.0mg Cr/ml Standard material : Metal chromium 99.9% up
Preparation : 1.000g of metal chromium is heated and dissolved with 20ml of aqua
method of regia and is diluted with water to 1000ml accurately after it has cooled.
solution
12. Cs (Cesium)
1.0mg Cs/ml Standard material : Cesium chloride (CsCl)
Preparation : 1.267g of cesium chloride is dissolved in water and is diluted to
method of 1000ml accurately with water after hydrochloric acid is added.
solution

13. Cu (Copper)
- 1.0mg Cu/ml Standard material : Metal copper 99.9% up
- Preparation : 1.000g of metal copper is heated and dissolved with nitric acid (1+1)
- method of : 30ml and is diluted to 1000ml accurately with 50ml of nitric acid (1+1)
- solution and water after it has cooled.
14. Fe (Iron)
- 1.0mg Fe/ml Standard material : Pure iron 99.9% up
- Preparation : 1.000g of pure iron is heated and dissolved with 20ml of aqua regia
- method of : and is diluted to 1000ml accurately after it has cooled.
- solution
15. Ge (Germanium)
- 1.0mg Ge/ml Standard material : Germanium oxide (GeO₂)
- Preparation : 1g of sodium hydroxide and 20ml of water are added to 1.439g of
- method of : germanium oxide and heated and dissolved. It is diluted to 1000ml
- solution accurately with water after it has cooled.
16. Hg (Mercury)
- 1.0mg Hg/ml Standard material : Mercury chloride (HgCl₂)
- Preparation : 1.354g of mercury chloride is dissolved in water and is diluted to
- method of : 1000ml accurately with water.
- solution
17. K (Potassium)
- 1.0mg K/ml Standard material : Potassium chloride (KCl)
- Preparation : Potassium chloride is heated at 600°C for about one hour and is cooled
- method of : in the desiccator. Its 1.907g is dissolved in water and diluted to 1000ml
- solution accurately with water after hydrochloric acid is added. Hydrochloric acid concentration is set at 0.1N.

18. Li (Lithium)
- 1.0mg Li/ml Standard material : Lithium chloride (LiCl)
- Preparation : 0.611g of lithium chloride is dissolved in water and diluted with water
method of to 1000ml accurately after hydrochloric acid is added. Hydrochloric
solution acid concentration is set at 0.1N.
19. Mg (Magnesium)
- 1.0mg Mg/ml Standard material : Metal magnesium 99.9% up
- Preparation : 1.000g of metal magnesium is heated and dissolved with hydrochloric
method of acid (1+5) 60ml and is diluted with water to 1000ml accurately after it
solution has cooled.
20. Mn (Manganese)
- 1.0mg Mn/ml Standard material : Metal manganese 99.9% up
- Preparation : 1.000g of metal manganese is heated and dissolved with 20ml of aqua
method of regia and is diluted to 1000ml accurately after it has cooled.
solution
21. Mo (Molybdenum)
- 1.0mg Mo/ml Standard material : Metal molybdenum 99.9% up
- Preparation : 1.000g of metal molybdenum is heated and dissolved with
method of hydrochloric acid (1+1) 30ml and a small quantity of nitric and is
solution diluted to 1000ml accurately with water after it has cooled.
22. Na (Sodium)
- 1.0mg Na/ml Standard material : Sodium chloride (NaCl)
- Preparation : Sodium chloride is heated at 600°C for about one hour and is cooled in
method of the desiccator. Its 2.542g is dissolved in water and is diluted with water
solution to 1000ml accurately after hydrochloric acid is added. Hydrochloric
acid concentration is set at 0.1N.

23. Ni (Nickel)

1.0mg Ni/ml Standard material : Metal nickel 99.9% up
Preparation : 1.000g of metal nickel is heated and dissolved with nitric acid (1+1)
method of 30ml and is diluted to 1000ml accurately with water.
solution

24. Pb (Lead)

1.0mg Pb/ml Standard material : Metal lead 99.9% up
Preparation : 1.000g of metal lead is heated and dissolved with nitric acid (1+1)
method of 30ml and is diluted with water to 1000ml accurately.
solution

25. Pd (Palladium)

1.0mg Pd/ml Standard material : Metal palladium 99.9% up
Preparation : 1.000g of metal palladium is heated and dissolved with 30ml of aqua
method of regia and is vaporized to dryness on a water bath.
solution 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 1000ml accurately. Hydrochloric acid
concentration is set at 0.1N.

26. Pt (Platinum)

1.0mg Pt/ml Standard material : Platinum 99.9% up
Preparation : 0.001g of platinum is heated and dissolved with 20ml of aqua regia
method of and vaporized to dryness on a water bath.
solution It is then dissolved with hydrochloric acid and diluted with water to
100 ml accurately. Hydrochloric acid concentration is set at 0.1N.

27. Sb (Antimony)

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

28. Si (Silicon)
- 1.0mg Si/ml Standard material : Silicon dioxide (SiO₂)
- Preparation : Silicon dioxide is heated at 700 to 800°C for one hour and cooled in
method of the desiccator. Its 0.214g is put in a crucible and is dissolved by mixing
solution 2.0h of sodium carbonate anhydrous and is diluted with water to 100ml
accurately.
29. Sn (Tin)
- 1.0mg Sn/ml Standard material : Metal tin 99.9% up
- Preparation : 0.500g of metal tin is added to 50ml of hydrochloric acid. Then heated
method of and dissolved at 50 to 80°C. After it has cooled, it is added to 200ml or
solution hydrochloric acid and diluted with water to 500ml accurately.
30. Sr (Strontium)
- 1.0mg Sr/ml Standard material : Strontium carbonate (SrCO₃)
- Preparation : 1.685g of strontium carbonate is dissolved with hydrochloric acid.
method of It is heated to remove carbon dioxide and is diluted to 1000ml
solution accurately with water after it has cooled.
31. Ti (Titanium)
- 1.0mg Ti/ml Standard material: Metal titanium 99.9% up
- Preparation : 0.500g of metal titanium is heated and dissolved with hydrochloric
method of acid (1+1) 100ml and is diluted with hydrochloric acid (1+2) to 500ml
solution accurately after it has cooled.
32. Tl (Thallium)
- 1.0mg Tl/ml Standard material : Metal thallium 99.9% up
- Preparation : 1.000g of metal thallium is heated and dissolved with nitric acid (1+1)
method of 20ml and is diluted with water to 1000ml accurately after it has cooled.
solution

33. V (Vanadium)

1.0mg V/ml Standard material : Metal vanadium 99.9% up

Preparation : 1.000g of metal vanadium is heated and dissolved with 30ml of aqua
method of regia and is concentrated to near dryness.

solution It is added to 20ml of hydrochloric acid and is diluted with water to
1000ml accurately after it has cooled.

34. Zn (Zinc)

1.0mg Zn/ml Standard material : Metal zinc 99.9% up

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

solution

4. Preparation of calibration curve and determination method

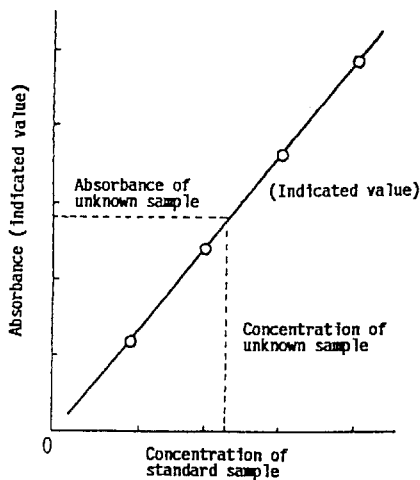
Atomic absorption spectrometry determines the sample by using the fact that sample concentrations are proportional to light absorbances in the atomization stage. (1) Calibration curve method and (2) Standard addition method are available as the determination method.

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 and 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

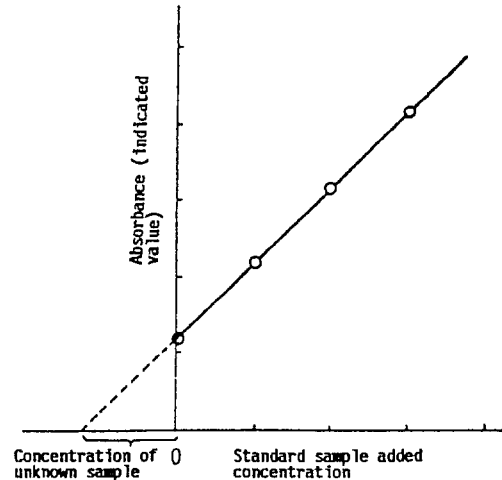


Fig. 4.1 Calibration curve

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 100ml measuring flasks are prepared and 10ml of the unknown sample of Mg concentration of $100 \times$ ppm is put in each of the above flasks. 0, 10, 20 and 30ml 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 100ml.

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.

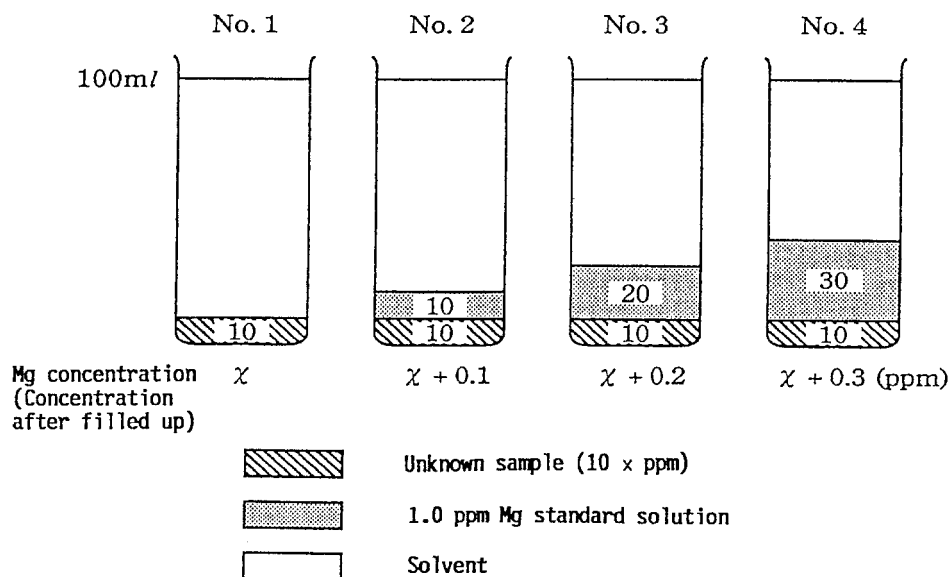


Fig. 4.2 Example preparation of standard solution in standard addition method

The advantage of this method is that it decrease 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 electrothermal 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°, the sensitivity drops to 1/20 and determination can be made to 20-fold the concentration of X the standard condition.

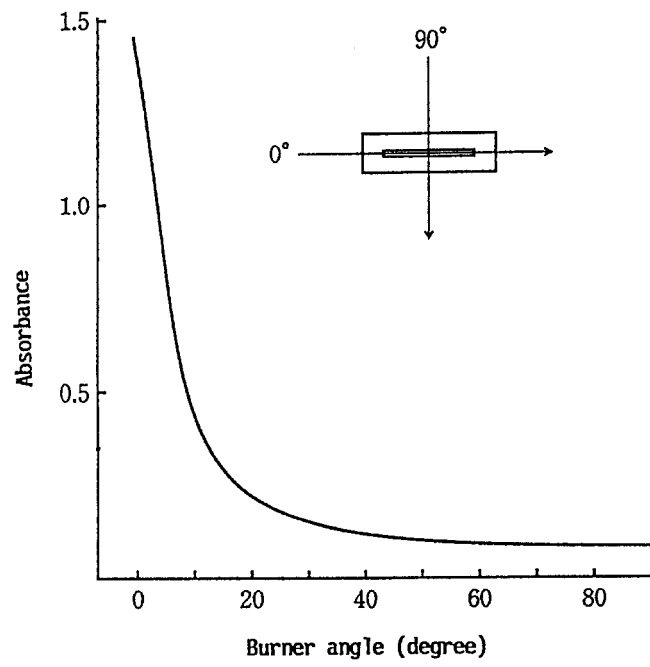


Fig. 4.3 Relation between burner angle and sensitivity

Table 4.1 1% absorption value in the flame and electrothermal atomic absorption methods

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

Element	Analysis line wavelength (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 ₂ H ₂	0.09		
Pr	495.1	N ₂ O-C ₂ H ₂	30		
Pt	265.9	Air-C ₂ H ₂	1.3	0.35	
Rb	780.0	Air-C ₂ H ₂	0.06		
Re	346.0	N ₂ O-C ₂ H ₂	12		
Ru	349.9	Air-C ₂ H ₂	0.6		
Sb	217.6	Air-C ₂ H ₂	0.33	1.6	0.25
Sc	391.2	N ₂ O-C ₂ H ₂	0.5		
Se	196.0	Ar-H ₂	0.5	0.7	0.28
Si	251.6	N ₂ O-C ₂ H ₂	1.3		0.57
Sm	429.7	N ₂ O-C ₂ H ₂	15		
Sn(1)	224.6	Air-C ₂ H ₂	2.0		2.0
Sn(2)	286.3	Air-C ₂ H ₂	5.0	5.5	
Sn(3)	224.6	N ₂ O-C ₂ H ₂	0.8		
Sn(4)	286.3	N ₂ O-C ₂ H ₂	2.0		
Sr	460.7	Air-C ₂ H ₂	0.06		
Ta	271.5	N ₂ O-C ₂ H ₂	15		
Tb	432.6	N ₂ O-C ₂ H ₂	12		
Te	214.3	Air-C ₂ H ₂	0.3	2.1	
Ti	364.3	N ₂ O-C ₂ H ₂	1.8	2.1	
Tl	276.8	Air-C ₂ H ₂	0.3		
V	318.4	N ₂ O-C ₂ H ₂	1.0	1.3	
W	255.1	N ₂ O-C ₂ H ₂	8.0		
Y	410.2	N ₂ O-C ₂ H ₂	3.0		
Yb	398.8	N ₂ O-C ₂ H ₂	0.1		
Zn	213.9	Air-C ₂ H ₂	0.011	0.03	
Zr	360.1	N ₂ O-C ₂ H ₂	15		
As(H)	193.7	Air-C ₂ H ₂	0.06		
Bi(H)	223.1	Air-C ₂ H ₂			
Sb(H)	217.6	Air-C ₂ H ₂	0.12		
Se(H)	196.0	Air-C ₂ H ₂	0.25		
Sn(H)	286.3	Air-C ₂ H ₂			
Te(H)	214.3	Air-C ₂ H ₂			

5. Interference in atomic absorption spectrophotometry

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 spectral 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 nm 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 occur in the wide wavelength range of the ultraviolet region. (Refer to Fig. 5.1)

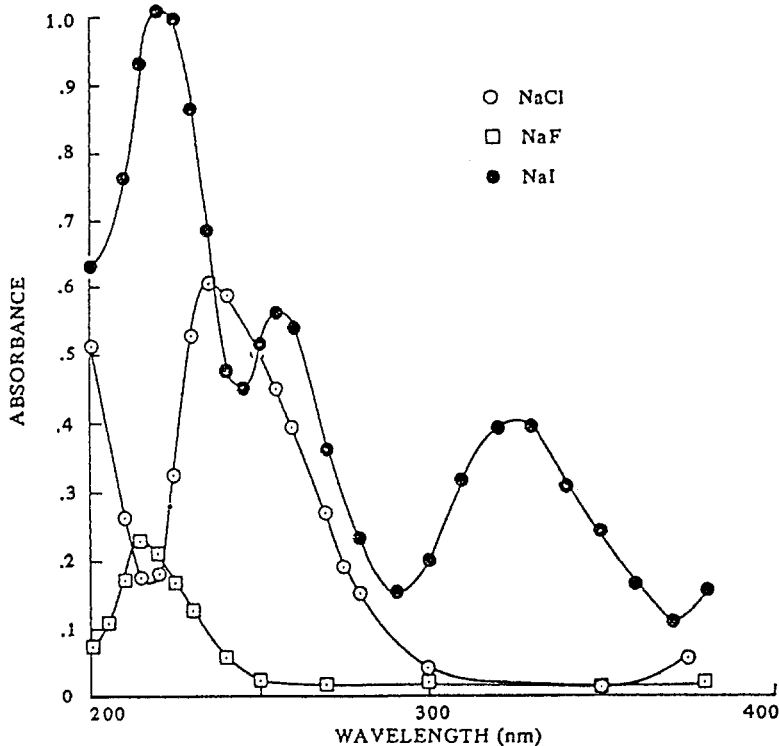


Fig. 5.1 Molecular absorption by sodium compound

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 concentrations.

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 $\pm 5\text{nm}$ 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 $\pm 5\text{nm}$. 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} Å 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 having half-width of about 10^{-2} Å. 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) Spectral interference caused by the analysis line of other element near the element.

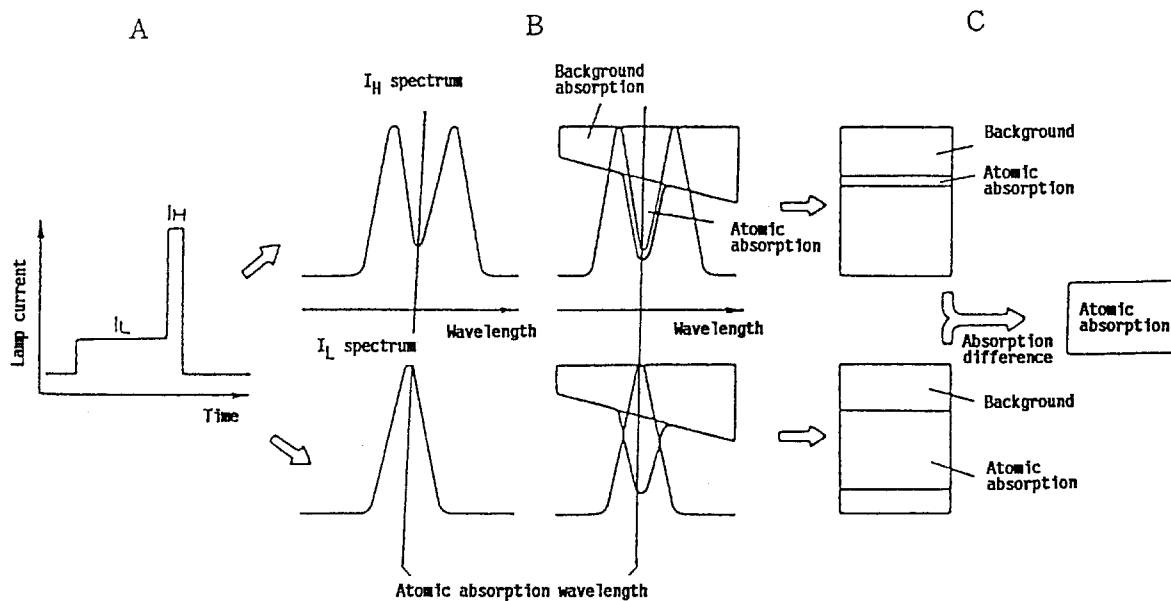


Fig. 5.2 Principle of background correction method by self reversal

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 raises 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

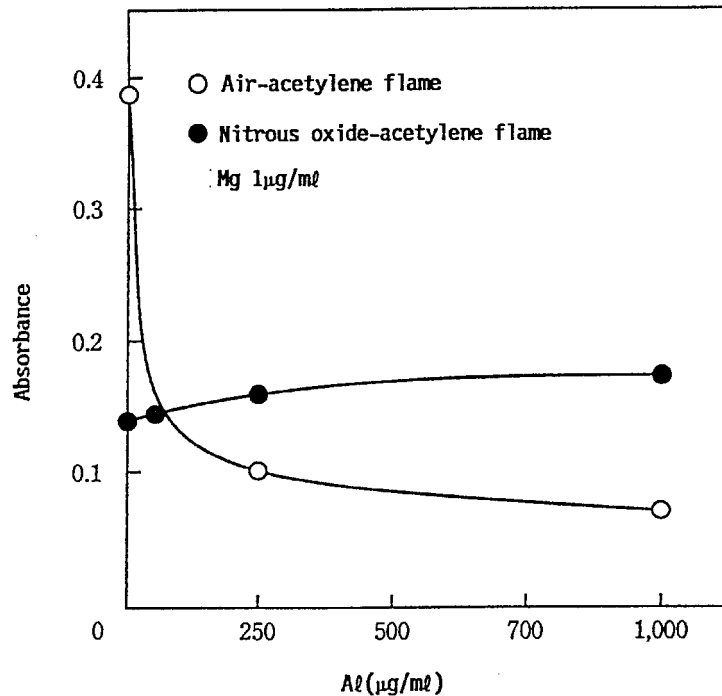
The sample introduced into the flame becomes free atoms by the heat, but part of them may be ionized.

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 Al react in the flame and $MgO \cdot Al_2O_3$ 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 Al, 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 spectrophotometry, Textbook
for Shimadzu course in atomic absorption spectrophotometry)**

Target element	Matrix modifier	Remarks
Cd	Pd (NO ₃) ₂ + NH ₄ NO ₃ (NH ₄) ₂ HPO ₄ + HNO ₃ Mg (NO ₃) ₂ (NH ₄) ₂ H ₂ PO ₄ + HNO ₃ or Mg (NO ₃) ₂	ppb level OK with blood, serum and urine. Addition of F ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ effective
Pb	Mg (NO ₃) ₂ La (NO ₃) ₃ Pd, Pt (μg level)	Coexistence with NaCl, KCl, MgCl ₂ , etc. prevents PbCl ₂ sublimation Effective by alloying HNO ₃ addition effective, high sensitivity attained by alloying
Hg	Sulfide + HNO ₃ HCl + H ₂ O ₂ K ₂ Cr ₂ O ₇ + Na ₂ S Au, Pt, Pd (μg level) Se Organic acid (Succinic acid, tartaric acid)	Volatization prevention as HgS } For prevention of reduction vaporization } Volatization prevention by amalgamation Used for soil
Tl	Pd, Pt, Ir La (NO ₃) ₃	Alloying Alloying
Bi	Pb	MIBK extract
Sn	Mg (NO ₃) ₂ , (NH ₄) ₂ HPO ₄ La (NO ₃) ₃ K ₂ WO ₄ , K ₂ MoO ₄ NH ₄ NO ₃ , (NH ₄) ₂ C ₂ O ₄	Use with ascorbic acid to prevent interference Effective by alloying Sensitivity improves remarkably but chloride interference exists No chloride interference

Target element	Matrix modifier	Remarks
Se	Mg (NO ₃) ₂ Pd, Pt, Cu, Al, Ni	Coexistence with Ni is effective (NiSe produced) Particularly Pb good, PdSe produced
As	Pd best, Mo, Zr, Ba also good La (NO ₃) ₃	Coexistence with Ni is effective Production of As ₂ O ₆ seems to be effective
Sb	Cu best, Ni, Pt also effective La (NO ₃) ₃	Alloying Alloying
Tl	Pd+HClO ₄ La (NO ₃) ₃	Coexistence with ascorbic acid is effective, Pd checks TlCl production Alloying
In	Pd La (NO ₃) ₃	Pd checks production of subliming InO Alloying
Ga	Ni	Ni checks GaO production and avoids inorganic matter interference
Zn	Succinic acid, oxalic acid	MaCl ₂ produces ZnCl ₂ and sublimes. Organic acid check it
P	La (NO ₃) ₃	Sensitivity improves by 6 times
Si, Al, Mn, Cu, Cd, Ba, Be, Cr	La (NO ₃) ₃	Effective with alloying