

**United States Department of Agriculture
Food Safety and Inspection Service, Office of Public Health Science**

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Title: Determination of Metals by ICP-MS and ICP-OES (Optical Emission Spectrometry)		
Revision: 06	Replaces: CLG-TM3.05	Effective: 11/05/18

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A. INTRODUCTION

1. Summary of Procedure

Sample is digested with concentrated nitric acid in a microwave digestion apparatus. The sample digest is diluted, fortified with internal standards, and analyzed using inductively coupled plasma mass spectrometry (ICP- MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) depending on the metals being monitored.

2. Applicability

This method is suitable for quantification of the analytes listed below in the following species: beef, pork, poultry, and fish of the order Siluriformes (catfish; muscle only).

Table 1 - Applicable Analytes ICP-MS

Metal	Applicable Matrices	ppb
Lead (Pb)	liver, kidney, muscle, processed products	≥ 25
Cadmium (Cd)	liver, kidney, muscle, processed products	≥ 10
Selenium (Se)	muscle, processed products	≥ 500
Manganese (Mn)	muscle, processed products	≥ 200
Molybdenum (Mo)	muscle, processed products	≥ 50
Thallium (Tl)	muscle, processed products	≥ 50
Cobalt (Co)	muscle, processed products	≥ 25
Arsenic (As)	muscle, processed products	50 - 200

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Table 2 - Applicable Analytes ICP-OES

Metal	Applicable Matrices	ppm
Iron (Fe)	muscle, processed products	≥ 30
Zinc (Zn)	muscle, processed products	≥ 30
Copper (Cu)	muscle, processed products	≥ 3
Nickel (Ni)	muscle, processed products	≥ 6
Aluminum (Al)	muscle, processed products	≥ 24
Boron (B)	muscle, processed products	≥ 4.8
Barium (Ba)	muscle, processed products	≥ 3.6
Chromium (Cr)	muscle, processed products	≥ 3.6
Vanadium (V)	muscle, processed products	≥ 3.6
Strontium (Sr)	muscle, processed products	≥ 3

Note: Refer to 21CFR for tolerance values set by FDA and 40CFR for tolerance values set by EPA.

B. EQUIPMENT

Note: Equivalent equipment may be substituted.

1. Apparatus

- a. Analytical balance - sensitive to 1 mg, Mettler, PG403-S
- b. MarsXpress Microwave and MarsXpress Digestion System, CEM.
- c. MarsXpress Microwave Digestion vessels - 55 mL capacity liners, vent plugs, and screw caps, CEM, cat. nos. 574125 and 212020.
- d. Vacuum Concentration/Drying apparatus - Microvap accessory set for MarsXpress system, CEM.
- e. Vacuum Scrubber Module and Dual Head Vacuum Pump, 120V/60Hz. Stirring rods (optional) - Teflon or polypropylene, Lab Depot, cat. no. F377390001.
- f. Volumetric flasks - polypropylene or polymethylpentane, 50, 100, 1000 mL, class A, Lab Depot cat. no. 5460P-50, 5640P-100, 5640P-1L .
- g. Volumetric flasks - glass, 10 - 1000 mL, as needed for preparation of standards, reagents class A, VWR cat. no. 89000-398 (10 mL) - 89000-412 (1000 mL).

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- h. Micropipettors - fixed or variable, covering ranges 10 - 5000 µL.
 - i. Bottles - polypropylene, 100 and 250 mL, Fisher, cat no. 02-893A, and 02-893B.
 - j. Centrifuge tubes - polypropylene, 50 mL and 15 mL, Fisher Scientific, cat. no. 14-432-22 and 14-959-49B.
 - k. Argon gas, high purity grade (99.99%).
 - l. Syringe filter (optional) - Acrodisc CR 13 mm, with 0.2 µm PTFE Membrane, Gelman Laboratory, VWR, cat no. 28143-982.
 - m. Milestone Trace Clean (optional).
 - n. Helium gas, ultra high purity ≥ 99.999%
 - o. Hydrogen gas, ultra high purity ≥ 99.999%
 - p. Stirring rods (optional)-Teflon or polypropylene, Lab Depot, cat. no. F377390001.
2. Instrumentation
- a. Inductively Coupled Plasma Mass Spectrometer - Agilent model 7500ce and or 7900, equipped with an Octapole Reaction System (ORS).
 - b. Inductively Coupled Plasma Spectrometer - Perkin-Elmer, model 5300DV, 7300DV and or 8300DV.

C. REAGENTS AND SOLUTIONS

Note: Equivalent reagents / solutions may be substituted. The maximum length of time that a working reagent shall be used is 1 year unless the laboratory has produced extension data.

1. Reagents
- a. Deionized water (DI water) - for cleaning only.
 - b. Millipure water - Deionized water polished to ASTM CAP/NCCLS Type 1 specifications or better (resistance ≥ 18 megaohms).
 - c. Nitric acid (HNO₃) - concentrated. Ultra-pure grade (Optima by Fisher Cat No. A467-500, or Double Distilled by GFS Cat No. 621) recommended. For samples, standards and reagents.
 - d. Nitric acid (HNO₃) - concentrated. Metal analysis or ICP-OES grade (e.g., OmniTrace by EMD Cat No. NX0407-1). For cleaning only.
 - e. Sodium Hydroxide (NaOH) – e.g. Fisher Cat No. S320-500.
 - f. Mass spectrometer tuning solution (1 & 10 µg/L) - Lithium, Yttrium, Cerium, Thallium, and Cobalt in 2% HNO₃, Cat No. 5185-5959 & 5184-3566, Agilent Technologies.

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g. Mass spectrometer PA tuning solution, Cat No. 5188-6524, Agilent Technologies.

2. Solutions

a. 25 - 50% NaOH solution (for evaporation scrubber):

Weigh 250 - 500 g of NaOH into a container with graduations and bring the volume up to approximately 1 L with water and mix.

b. 2% HNO₃ solution:

Dilute concentrated HNO₃ 1:50 with millipure water (e.g., 20 mL/1L). Prepare and store in polypropylene bottles.

Note: Additional HNO₃ concentrations may be necessary based on commercial standards.

D. STANDARD(S)

Note: Equivalent standards / solutions may be substituted. Purity and counterions are to be taken into account when calculating standard concentrations. In-house prepared standards shall be assigned an expiration date that is no later than the stability stated in the method. The maximum length of time that an in-house prepared standard shall be used is 1 year unless the laboratory has produced extension data.

Note: All standards and solutions may be stored at room temperature.

1. Commercial/Custom Mixed Standards

Table 3 - Analytical Standard Information - ICP-MS

MS Mixed Stock Standard	Concentration (µg/mL)	Supplier	Catalog No.
Arsenic	100	SCP Science	AQ0-090-411
Cadmium	100	SCP Science	AQ0-090-411
Cobalt	100	SCP Science	AQ0-090-411
Lead	100	SCP Science	AQ0-090-411
Manganese	100	SCP Science	AQ0-090-411
Molybdenum	100	SCP Science	AQ0-090-411
Selenium	100	SCP Science	AQ0-090-411
Thallium	100	SCP Science	AQ0-090-411
MS Fortification Stock Standard	Concentration (µg/mL)	Supplier	Catalog No.
Arsenic	50	SCP Science	AQ0-090-421
Cadmium	5	SCP Science	AQ0-090-421
Cobalt	12.5	SCP Science	AQ0-090-421

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Lead	12.5	SCP Science	AQ0-090-421
Manganese	100	SCP Science	AQ0-090-421
Molybdenum	25	SCP Science	AQ0-090-421
Selenium	250	SCP Science	AQ0-090-421
Thallium	25	SCP Science	AQ0-090-421
Single Stock Standard	Concentration (µg/mL)	Supplier	Catalog No.
Selenium	1000	SCP Science	140-051-341
Mixed Internal Standard	Concentration (µg/mL)	Supplier	Catalog No.
Bismuth	50	SCP Science	600-144-303
Germanium	50	SCP Science	600-144-303
Indium	50	SCP Science	600-144-303
Scandium	50	SCP Science	600-144-303
Yttrium	50	SCP Science	600-144-303

Table 4 - Analytical Standard Information - ICP-OES

OES Mixed Stock Standard	Concentration (µg/mL)	Supplier	Catalog No.
Aluminum	400	SCP Science	600-144-305
Barium	60	SCP Science	600-144-305
Boron	80	SCP Science	600-144-305
Chromium	60	SCP Science	600-144-305
Copper	50	SCP Science	600-144-305
Iron	500	SCP Science	600-144-305
Nickel	100	SCP Science	600-144-305
Strontium	50	SCP Science	600-144-305
Vanadium	60	SCP Science	600-144-305
Zinc	500	SCP Science	600-144-305

Table 5- Calibration Curve Verification (CCV) Standards

Quality Control CCV Standards	Concentration (µg/mL)	Supplier	Catalog No.
Strontium	100	Inorganic Ventures	MSSR-100PPM
IV-7	100	Inorganic Ventures	IV-7
IV-19	100	Inorganic Ventures	IV-19

Note: Single standards are also usable.

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2. Preparation of Standard Solution(s)

Important: Metals may be leached from glass by nitric acid. Store all standard solutions in polypropylene or other inert containers. If glassware is used, it should be cleaned with nitric acid and dedicated for trace metals analyses. Standards prepared in glassware should be used immediately or transferred to suitable containers for storage.

a. Internal standard (ISTD), (5000 µg/L):

Combine in a 500 mL volumetric flask 50 mL of the Mixed Internal Standard Stock Solution with 10.0 mL of nitric acid and bring to volume with water.

Note: Other internal standards can be used as long as the element is not contained in the sample, the mass number is similar to that of the analyte, and the ionization potential is similar to that of the analyte.

b. Calibration Standards - ICP-MS

Calibration standards are required for constructing a multipoint standard curve covering the range of analyte concentrations anticipated in samples.

Prepare intermediate standards by making dilutions of commercially available standard solutions into a concentration of HNO₃ similar to the commercial solution.

i. MS Intermediate Standard 1 (1000 µg/L):

Combine in a 100 mL volumetric flask 1.0 mL of MS Mixed Standard Stock Solution with 2.0 mL nitric acid and bring to volume with water.

ii. MS Intermediate Standard 2 (100 µg/L):

Combine in a 50 mL volumetric flask 5.0 mL of the 1000 µg/L MS Intermediate Standard 1 with 1.0 mL nitric acid and bring to volume with water.

iii. Selenium Intermediate Standard (1000 µg/L):

Combine in a 50 mL volumetric flask 50 µL of the Selenium Standard Stock Solution with 1.0 mL nitric acid and bring to volume with water.

Prepare calibration standards by making appropriate dilutions of intermediate standards with 2% HNO₃ and adding sufficient 5000 µg/L ISTD to result in a final ISTD concentration of 5 µg/L. Prepare these standards using polymeric volumetric flasks.

The Table below lists some suggested concentrations for calibration standards and recommended volumes and concentrations of solutions required.

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Table 6 - Calibration Standards - ICP-MS

Standard Conc. (µg/L)	5000 µg/L Metals Internal Std. (µL)	1000 µg/L MS Intermediate Std. 1 (µL)	100 µg/L MS Intermediate Std. 2 (µL)	1000 µg/L Se Intermediate Std. (µL)	Nitric Acid (mL)	Final Volume (mL)
0.0	500	—	—	—	10	500
0.10	250	—	250	—	5	250
0.25	250	—	625	—	5	250
0.50	250	—	1250	—	5	250
1.00	250	—	2500	—	5	250
2.50	250	625	—	—	5	250
5.00	250	1250	—	—	5	250
10.0	250	—	—	2500	5	250
20.0	250	—	—	5000	5	250

c. Fortification Standard – ICP-MS

Combine in a 100 mL volumetric flask 2.0 mL of the MS Fortification Standard Stock Solution, 2.0 mL of nitric acid and bring to volume with water. The Fortification Standard added to control tissue is equivalent to between 1 × MLA to 2 × MLA of the metals based on a 0.5 g sample weight. Final concentrations are calculated based on the dilution of the stock standard.

Table 7 - Typical Fortification Standard Concentration (ICP-MS)

	As	Cd	Co	Pb	Mn	Mo	Se	Tl
MS Fortification Standard (µg/L)	1000	100	250	250	2000	500	5000	500

d. Quality Control Standards – ICP-MS

Prepare Quality Control standards from commercially available standard solutions obtained from a *different source* than those used to prepare Calibration Standards. Two levels of quality control standard must be prepared:

i. Intermediate CCV Standard

Combine in a 50 mL volumetric flask 50 µL of the IV-19 solution with 1.0 mL nitric acid and bring to volume with water.

ii. CCV Low (0.40 µg/L):

Combine in a 500 mL volumetric flask 2.0 mL Intermediate CCV Standard, 500 µL of Internal Standard, 10.0 mL nitric acid and bring to volume with water.

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iii. CCV High (2.0 µg/L)

Combine in a 500 mL volumetric flask 10.0 mL Intermediate CCV Standard, 500 µL of Internal Standard, 10.0 mL nitric acid and bring to volume with water.

e. Calibration Standards and Fortification Standard - ICP-OES

Add components to the stated size volumetric flasks in the following table to produce a calibration curve and/or fortification standard.

Table 8 – Calibration and Fortification Standards – ICP-OES

Standard Level	5000 µg/L Metals Internal Std. (µL)	OES Mixed Std. Stock Solution (µL)	Nitric Acid (mL)	Final Volume (mL)
Cal. Blank	500	0	10	500
1	250	150	5	250
2	250	300	5	250
3	250	450	5	250
4	250	600	5	250
Fort. Std.	0	10000	5	100

Table 9 – Typical ICP-OES Calibration and Fortification Standard Concentrations (µg/mL)

	Al	Ba	B	Cr	Cu	Fe	Ni	Sr	V	Zn
Cal. Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.24	0.04	0.05	0.04	0.03	0.30	0.06	0.03	0.04	0.30
2	0.48	0.07	0.10	0.07	0.06	0.60	0.12	0.06	0.07	0.60
3	0.72	0.11	0.14	0.11	0.09	0.90	0.18	0.09	0.11	0.90
4	0.96	0.14	0.19	0.14	0.12	1.20	0.24	0.12	0.14	1.20
Fort. Std.	40	6	8	6	5	50	10	5	6	50

f. Quality Control Standards - ICP-OES

Prepare Quality Control standards from commercially available standard solutions obtained from a *different source* than those used to prepare Calibration Standards. Two levels of quality control standard must be prepared:

i. CCV Low (0.05 µg/mL)

Combine in a 500 mL volumetric flask 250 µL of Strontium stock solution, 250 µL IV-7, 250 µL IV-19, 500 µL Internal Standard, 10.0 mL nitric acid and bring to volume with water.

ii. CCV High (0.50 µg/mL)

Combine in a 500 mL volumetric flask 2500 µL of Strontium stock solution, 2500 µL IV-7, 2500 µL IV-19, 500 µL Internal Standard, 10.0 mL nitric acid and bring to volume with water.

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E. SAMPLE PREPARATION

Note: Since trace amounts of analyte metals are ubiquitous in the environment and may be present in dust particles, efforts should be made to avoid external contamination. All areas/materials involved in sample preparation and analysis should be kept as dust-free as possible to minimize the chance of contamination.

Samples must be thoroughly blended to assure uniformity prior to removal of a test portion.

F. ANALYTICAL PROCEDURE

1. Preparation of Controls and Samples

- a. Weigh homogenized samples, and blank tissue sufficient to prepare the negative control(s), positive control(s), and check samples (0.5 ± 0.010 g for muscle tissues, 0.5 - 1 g for liver and kidney¹) for both ICP-MS and ICP-OES to the nearest 0.001 g into a clean² microwave vessel liner, using separate vessels for ICP-MS and ICP-OES controls. Teflon or polypropylene stirring rods may be used to manipulate samples.

Note: Truly blank tissues may not be available. Use previously analyzed tissues having low analyte levels for this purpose.

¹Caution! Mixing sample types or sample weights may produce unacceptably large variations in pressures developed during digestion, possibly resulting in damage to vessels if unvented caps are used. In order to maintain relatively constant digestion conditions in all unvented vessels, analyst should digest like quantities of similar sample matrices in each batch.

²Vessel liners, caps, stoppers, and tubing must be cleaned after each use to reduce the possibility of cross-contamination. Refer to Section J.2 for recommended cleaning procedure.

- b. Prepare positive control(s) by adding Fortification Standard to the tissue blank within the quantitation range. e. g.
 - i. ICP-MS: fortify with 75 μ L of D.2.c
 - ii. ICP-OES: fortify with 300 μ L of D.2.e

2. Extraction Procedure

- a. Microwave Digestion
 - i. Add 5 mL of concentrated HNO₃, Ultra-pure grade, to each vessel.
 - ii. Assemble the vessel according to the manufacturer's instructions.
 - iii. Place assembled vessels into the microwave according to the manufacturer's instructions.

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- iv. Program oven with parameters demonstrated to safely and effectively digest samples (producing a clear digest when diluted). Recommended parameters are listed in the table below. It may be necessary to adjust these parameters to accommodate variations between individual instruments.

Power:	1600 Watts*
Ramp time:	12 minutes
Final temperature:	180 °C
Temperature hold time:	10 minutes
Cool down time:	10 minutes

*If there are less than eight vessels in the microwave the wattage can be lowered.

- v. Initiate oven program and digest samples.
- vi. Allow vessels to cool, then transfer to a fume hood and allow vessels to equilibrate to room temperature.
- vii. Slowly open the vent fittings and vent to atmospheric pressure, then disassemble vessels.
- b. Microwave Evaporation
- i. Place vessel liners into the evaporation carousel and assemble according to the manufacturer's instructions. Note: Manufacturer recommends use of PTFE syringe filters with the evaporation manifold for trace metal analysis (optional).
- ii. Place the evaporation assembly into the microwave.
- iii. Program oven to reduce solution volumes to approximately 1 mL. Typical program parameters are listed below. Parameters may be adjusted.

Power:	800 Watts
Ramp time:	5 minutes
Final temperature:	100 °C
Temperature hold time:	3 minutes*
Cool down time:	10 minutes

*Typical value required when 8 vessels are used. Hold times required to achieve a final volume of 1 mL for any given number of vessels must be determined experimentally.

Note: If the microwave is capable of determining an evaporation plateau temperature, a temperature drop of $\Delta T \approx 7$ °C may be used to control the final volume. This approach is more variable, but does not require

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adjustment for tissue type, tissue weight, or number of samples.

- iv. Initiate oven program and evaporate samples.
- v. Once vessels have cooled to room temperature, remove the evaporation assembly from the oven and dismantle. Flush the evaporation manifold with DI water.

c. Extraction Preparation

- i. If the solution volume remaining in the vessel liner is <1 mL, add concentrated HNO₃ to bring volume to approximately 1 mL. Note: residual acid volumes of up to 2.5 mL are acceptable, but should be avoided if possible. Pour extract solution into a 50 mL plastic tube containing approximately 10 mL millipure water.
- ii. Quantitatively transfer residual digest by rinsing the liner 3 - 4 times with millipure water, adding each rinse to the extract in the tube. Keep total rinse volume < 35 mL.

Add 50 µL of 5000 µg/L ISTD solution to the extract.

- iii. Bring extract volume to 50 mL with millipure water.
- iv. Cap tube and invert several times to mix.

Note: The percentage of dissolved solids in the 50 mL extract, which is higher than that recommended by instrument manufacturer, can be reduced by increasing the dilution volume. Analyst must balance detrimental effects of high dissolved solids content (matrix effects, instrument contamination) against detrimental effects resulting from environmental contamination and lower analyte concentrations when considering this. If additional dilutions are made, care must be taken to maintain acid strength at ~2% and ISTD concentration at 5 µg/L. Adjust standard curve concentrations accordingly, if necessary.

- v. Place sample and QC solutions on autosampler for analysis.

3. Instrumental Settings - ICP-MS Analysis

Note: The instrument parameters may be optimized to ensure system suitability.

a. Tuning

Prior to sample analysis check the instrument's tuning parameters by analyzing the Mass Spectrometer Tuning Solution as specified by the manufacturer. Check the sensitivity, % RSD, % oxide, % doubly charged, peak shape, and resolution.

b. ICP-MS Parameters

Set up instrument to monitor isotopes of appropriate metals, internal standards and modes. Each quantitated isotope is specified with a minimum integration time and may be optimized.

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Table 10. ICP- MS Metal Isotopes

Metal	Isotope <i>*Isotope used for quantitation</i>	Gas Mode	Integration Time (sec) /Point (*Isotope)
Manganese	55*	He	0.10
Cobalt	59*	He	0.10
Selenium	78*, 82	H ₂	0.30
Molybdenum	95, 98*	He	0.10
Cadmium	111*, 112,114	He	0.20
Thallium	203, 205*	He	0.10
Lead	206*, 207*, 208*	He	0.10
Arsenic	75*	He	0.20

Note: These metals can be analyzed in no gas mode (no reaction cell), or another gas mode, but may require the use of interference correction equation(s).

Table 11. ICP-MS Internal Standard Isotopes

Internal Standard	Isotope	Integration Time (sec) /Point
Scandium	45	0.10
Gallium	69, 71	0.10
Germanium [H ₂ Mode]	72	0.30
Germanium [He Mode]	72	0.20
Yttrium	89	0.10
Rhodium	103	0.10
Indium	115	0.20
Terbium	159	0.10
Bismuth	209	0.10

Note: These metals can be analyzed using alternate internal standards/isotopes as necessary.

c. Instrument calibration

- i. Analyze a calibration blank followed by at least 3 calibration standards (D.2.b) covering the range of interest. Using linear regression analysis, plot relative response (response relative to ISTD response) vs. concentration in µg/L and determine slope (m), intercept (b), and correlation coefficient (r) of the calibration curve. This can be

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automatically performed by the ICP-MS software. Correlation coefficient r must be ≥ 0.995 , or calibration must be repeated.

- ii. Analyze the calibration blank and a QC standard (D.2.d) immediately after the calibration curve. The response of the blank should be similar to that observed when initially analyzed. The calculated metals concentrations in the QC standard must be within $\pm 12\%$ of their accepted value. If these conditions are not met, the calibration sequence must be repeated until results are acceptable.
 - d. Instrument Wash (Optional)

0.1% Triton-X or 0.1% Citranox detergent solutions may be utilized before, during and after analysis to further reduce tubing obstruction caused by lipid precipitate found in sample extracts. A water rinse of 2 to 5 minutes is necessary to remove to detergent solution.
4. Instrumental Settings - ICP-OES Analysis
- Note: The instrument parameters may be optimized to ensure system suitability.
- a. Mn check
 - i. Prior to sample analysis check the instrument's stability by analyzing a 1 ppm Mn solution and collecting 10 replicates. Check the sensitivity, and % RSD should be $\leq 2\%$.
 - ii. If these parameters are outside the manufacturer's specifications or QC requirements, examine pump tubing, drain tubing, torch condition, etc., and then reanalyze check solution.
 - b. ICP-OES Parameters

Set up instrument to monitor responses of appropriate metals, and selected internal standards.

Table 12. ICP-OES Wavelengths

Metal	Analytical Wavelength	Internal Std
Iron	239.562	Scandium
Zinc	213.857	Scandium
Copper	324.752	Yttrium
Nickel	231.604	Yttrium
Aluminum	396.153	Yttrium
Boron	249.772	Yttrium
Barium	233.527	Yttrium

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Metal	Analytical Wavelength	Internal Std
Chromium	267.716	Yttrium
Vanadium	292.402	Yttrium
Strontium	460.733	Yttrium

Note: These metals can be analyzed using alternate wavelengths and/or internal standards as necessary.

Table 13. ICP-OES Internal Standard Wavelengths

Internal Standard	Wavelength
Scandium	361.383
Gallium	294.364
Germanium	209.426
Yttrium	371.029
Rhodium	233.477
Indium	230.606
Terbium	350.917
Bismuth	223.061

- c. Instrument calibration
 - i. Analyze a calibration blank followed by at least 3 calibration standards (D.2.e) covering the range of interest. Using linear regression analysis, plot relative response (response relative to ISTD response) vs. concentration in $\mu\text{g/mL}$ and determine slope (m), intercept (b), and correlation coefficient (r) of the calibration curve. This can be automatically performed by the ICP-OES software. Correlation coefficient r must be ≥ 0.995 , or calibration must be repeated.
 - ii. Analyze the calibration blank (optional) and a QC standard (D.2.f.) immediately after the calibration curve. The relative response of the blank should be similar to that observed when initially analyzed. The calculated metals concentrations in the QC standard must be within $\pm 12\%$ of their accepted value. If these conditions are not met, the calibration sequence must be repeated until results are acceptable.

5. Injection sequence / Sample Set (ICP-MS and ICP-OES)
 - a. Calibration blanks (optional for ICP- OES) and QC standards must be included in the sample analysis sequence to verify instrument performance over the course of the run.

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- b. If response of any sample exceeds highest standard in the calibration curve, make an appropriate dilution in 2% HNO₃ and add ISTD to maintain a 5 µg/L concentration, then re-analyze.
- c. A sample set for both ICP-MS and ICP-OES consists of the following:
 - Note: Each sample set must contain one QA sample/20 samples.
 - i. Reagent Blank (optional)
 - ii. Negative control.
 - iii. Positive control(s).
 - iv. Samples.

G. CALCULATIONS / IDENTIFICATION (ICP-MS and ICP-OES)

Note: Instrument software can be programmed to perform all necessary calculations.

- 1. Using values for m, b determined for the calibration curve (F.3.c), determine selected analyte concentration (C_E, in µg/L) in any extract having a relative response R using:

$$C_E (\mu\text{g/L}) = C_E, \mu\text{g/L} = (R-b)/m$$

Note: If sample is found to contain molybdenum, instrument software must be set to compensate for contribution of molybdenum oxide to the 111 isotope used for quantitation of cadmium in the sample.

- 2. Calculate selected analyte concentrations in digested controls and samples (C_S) using:

$$C_S (\text{ppb}) = \frac{C_E \times V_E \times D}{W}$$

Where

C_E = Analyte concentration in final extract, in µg/L

V_E = Final sample extract volume in milliliters

D = Dilution factor (Diluted volume/aliquot volume), if secondary dilution was made.

W = Sample Weight in grams.

- 3. Calculate Relative % Difference (RPD) for duplicate results using:

$$\text{RPD} = \frac{|C1 - C2| \times 200}{(C1 + C2)}$$

Where:

C1 = first duplicate's concentration.

C2 = second duplicate's concentration.

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4. Calculate recoveries of fortified controls and check samples using

$$\%Rec = \frac{(C_F - C_B) \times W \times 100}{V_{FS} \times C_{FS}}$$

Where

C_F , C_B = Analyte concentrations determined for the fortified sample and the blank tissue from which it was prepared, in ppb (ng/g).

W = Weight of fortified control, in grams.

V_{FS} = Volume of fortification standard added, in mL.

C_{FS} = Concentration of fortification standard, in $\mu\text{g/L}$.

H. SAFETY INFORMATION AND PRECAUTIONS

1. Required Protective Equipment - Safety glasses, lab coat, protective gloves.
2. Hazards

<i>Procedure Step</i>	<i>Hazard</i>	<i>Recommended Safe Procedures</i>
Nitric Acid	Strong oxidizer. May be fatal if swallowed or inhaled. Extremely corrosive. Contact with skin or eyes may cause severe burns and permanent damage.	Perform operations using concentrated acid in fume hood. Use protective eyewear, gloves and clothing. Store in approved acid safety cabinet away from basic or other reactive materials.
Microwave Digester	Possible explosion hazard	Follow manufacturer recommendations
Metals Standards	Poisonous if ingested.	Do not pipet by mouth

3. Disposal Procedures
Follow local, state and federal guidelines for disposal.

I. QUALITY ASSURANCE PLAN

1. Performance Standard

Table 14 - Performance Standard ICP-MS

<i>Analyte</i>	<i>Acceptable Recovery (%)</i>
Arsenic	81-136
Cadmium	67-127

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<i>Analyte</i>	<i>Acceptable Recovery (%)</i>
Cobalt	79-107
Lead	86-110
Manganese	80-112
Molybdenum	86-116
Selenium	76-145
Thallium	94-112

Table 15 - Performance Standard ICP-OES

<i>Analyte</i>	<i>Acceptable Recovery (%)</i>
Iron	85 - 115
Zinc	83 - 121
Copper	80 - 118
Nickel	88 - 110
Aluminum	86 - 120
Boron	80 - 109
Barium	87 - 116
Chromium	89 - 109
Vanadium	90 - 111
Strontium	94 - 153

For each sample set:

- a. The instrument calibration meets specifications in section F.3.c. and F.4.c.
- b. For set acceptance, 90% of the monitored analytes in the positive control must meet specifications. To report a positive sample, the analytes of interest in the positive control must meet specifications.
- c. If a positive control duplicate is run, the calculated RPD is $\leq 20\%$.
- d. All calibration blanks injected show consistent responses, and the first QC standard is within $\pm 12\%$ of the accepted value.
- e. For ICP-MS perform the following: for each sample within the set, the internal standard response is within $\pm 50\%$ of the average instrument calibration internal standard response.

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2. Critical Control Points and Specifications

None known

3. Intralaboratory Check Samples

a. System, minimum contents.

- i. Frequency: One per week per analyst when samples analyzed.
- ii. Records are to be maintained.

b. Acceptability criteria.

Refer to I. 1.

If unacceptable values are obtained, then:

- i. Investigate following established procedures.
- ii. Take corrective action as warranted.

4. Sample Condition upon Receipt: Cold

J. APPENDIX

1. References

- a. Agilent 7500 ICP-MS Hardware Manual, G1833-90004, January 2001.
- b. CEM XP-1500 Plus Vessel Accessory Sets and Autovent Option Instruction for Use, 600493, Rev. 5, 8/01.
- c. CEM Vacuum Concentration/Drying Accessory Set Instructions for Assembly and Use, 600484, Rev. 1, 6/99.
- d. CEM Mars Operation Manual, 600122, Rev 2, February, 2006.
- e. EPA Method 6020, Inductively Coupled Plasma-Mass Spectrometry, Revision 0, September 1994.
- f. Perkin Elmer 5000 Series Hardware Guide, 0993-6762, D, February 2007.

2. Cleaning Vessel Liners

The following procedures are suitable for removal of residual adsorbed residues from Teflon liners used in this method. Other procedures are available and may be used if demonstrated to be effective.

Option 1

- a. Add approximately 10 mL of conc. HNO₃ (metal analysis grade) to each digestion vessel liner.

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- b. Assemble vessels as specified by manufacturer.
- c. Place in microwave.
- d. Digest at 600W, ramp to 150 °C over 10 minutes, then hold at temperature for 10 minutes.
- e. Cool vessels to room temperature, then disassemble.
- f. Rinse vessel liners and caps with millipure water several times to remove all traces of acid.
- g. Place in a clean environment to dry.
- h. Reference: CEM VesselCleaning09.doc, 04/09

Option 2

Using a Milestone Trace Clean apparatus and conc. metal analysis grade HNO₃:

- a. Place the microwave vessel liners and caps into the apparatus.
- b. Start the method program as per the manufacturer suggestion.
- c. After the apparatus has cooled, remove the liners and caps.
- d. Rinse several times with Ultrapure water to remove all traces of acid.
- e. Place in a clean environment to dry.

K. APPROVALS AND AUTHORITIES

- 1. Approvals on file.
- 2. Issuing Authority: Director, Laboratory Quality Assurance Staff.