



A Honeywell Company

Metals in Miscellaneous Samples by ICP-OES

UOP Method 714-07

Scope

This method is for determining metals in samples of unknown composition such as residues and deposits. Aluminum (Al), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), sodium (Na), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr) are quantitatively determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). Concentrations determined generally cover the range of 0.02 to several mass-%, see Table 1. Sample dilution extends the working range for major (matrix) components. If requested, additional elements can be determined, if the sample preparation method is appropriate for the additional elements.

Table 1
Applicable Concentration Ranges, Mass-%

<u>Element</u>	<u>Range</u>	<u>Element</u>	<u>Range</u>
Aluminum	0.02 - 2.5	Manganese	0.01 - 2.5
Cadmium	0.02 - 1.25	Molybdenum	0.03 - 2.5
Calcium	0.01 - 10	Nickel	0.03 - 2.5
Chromium	0.03 - 2.5	Potassium	0.10 - 2.5
Cobalt	0.02 - 2.5	Sodium	0.01 - 10
Copper	0.01 - 1.25	Tin	0.05 - 2.5
Iron	0.02 - 50	Titanium	0.01 - 1.25
Lead	0.05 - 2.5	Vanadium	0.01 - 5
Magnesium	0.01 - 10	Zinc	0.02 - 2.5

Barium (Ba) and silicon (Si) cannot be determined by this method due to the acid treatment of the samples. Alpha-alumina will not dissolve in the acid media used in this method.

An alternative microwave-based dissolution technique is described in the *Appendix*. Silicon can be determined using the microwave-based dissolution technique; and instructions for the analysis of silicon are included.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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References

ASTM Method D 1193, "Specification for Reagent Water," www.astm.org

UOP Method 954, "Loss on Ignition for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The samples are decomposed by digestion with sulfuric and hydrofluoric acids. The addition of hydrofluoric acid and heating the digest volatilizes silica. Additional acid treatments may be necessary, depending upon the sample matrix. Scandium is added to the solution as the internal standard and the sample solutions are analyzed by ICP-OES calibrated with appropriate, matrix(acid)-matched standards.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Beaker, Teflon™, PTFE, 250-mL, Fisher Scientific, Cat. No. 02-593-5B

Bottle, wash, polyethylene, 500-mL, VWR, Cat. No. 16651-187

Sample grinding equipment

Balls, grinding, 11.1-mm (7/16-inch), tungsten carbide, SPEX Industries, Inc., Cat. No. 8004A, or equivalent

Container, grinding, 57 x 64 mm (2-1/4 x 2-1/2 inches), tungsten carbide, SPEX Industries, Inc., Cat. No. 8004, or equivalent

Mixing mill, shaker type, SPEX Industries, Inc., Cat. No. 8000

Mortar and pestle, Agate, VWR, Cat. No. 50410-060

Cylinders, graduated, polypropylene, Class B, 10- and 100-mL, Fisher Scientific, Cat. Nos. 08-572A and -572D, respectively

Flasks, volumetric, Class B, Nalgene polypropylene, 100, 200, and 500-mL capacity, Fisher Scientific, Cat. Nos. 10-198-50B, -50C, and -50E respectively, several of each required

Hot plate, stirring, variable heat to at least 400°C

Pipet, microliter, 2500-μL capacity, Rainin Instrument Co., Cat. No. EP-2500

Pipet, 10-mL capacity, Rainin Instrument Co., Cat. No. EP-10ML

Pipets, volumetric, transfer, Class A, 1-, 2-, 5-, 10-, 20-, 25-, 40-, and 50-mL, Fisher Scientific, Cat. Nos. 13-650-2B, -2C, -2F, -2L, -2N, -2P, -2R, and -2S, respectively

Regulator, argon, two-stage, high-purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Regulator, nitrogen, two-stage, high-purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Spectrometer, Inductively Coupled Plasma-Optical Emission Spectrometer, computer controlled, having sufficient resolving power and dispersion to separate the analytical lines in the 160-800 nm region. The computer must be capable of performing background corrections, blank corrections, and weight/volume and dilution corrections. A commercial grating spectrometer with a band pass of 0.018 nm or less in the first order is satisfactory. PerkinElmer Optima 5300 V

Watch glass, Teflon, PTFE, 75-mm diameter, Fisher Scientific, Cat. No. 02-610-5C

Weighing scoop, Fisher Scientific, Cat. No. 01-914-36

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean ASTM D 1193 Type I reagent grade water.

Argon, 99.995% minimum purity, ICP feed gas

Hydrochloric acid, concentrated

Hydrofluoric acid, concentrated

Nitrogen, 99.99% minimum purity, ICP optics purge gas

Pipet tips, disposable, for EP-2500 microliter pipet, Rainin Instrument Co., Cat. No. RC-2500

Pipet tips, disposable, for EP-10ML pipet, Rainin Instrument Co., Cat. No. RC-2500

Pipets, disposable, polyethylene, general purpose, 1.7-mL, VWR, Cat. No. 16001-174

Scandium solution, aqueous, 1000 µg/mL, SPEX Industries, Inc., Cat. No. PLSC-2

Standard solutions of metals, Fe, Ni, V, Ca, Mg, Mn, Cr, Sn, Cu, Zn, Ti, Pb, Na, Mo, Co, Al, Cd, K, Sr, and Zr solutions of 1000 µg/mL concentrations, SPEX Industries, Inc., Cat. Nos. PLFE-2, PLNI-2, PLV-2, PLCA-2, PLMG-2, PLMN-2, PLCR-2, PLSN-2, PLCU-2, PLZN-2, PLTI-2, PLPB-2, PLNA-2, PLMO-2, PLCO-2, PLAL-2, PLCD-2, PLK-2, PLSR-2X, and PLZR3-2X respectively

Sulfuric acid, concentrated

Nitric acid, concentrated

Water, ASTM D 1193 Type I reagent grade

Procedure

Caution: All steps involving additions of acids and heating of samples must be performed in a properly operating fume hood, and appropriate personal protective equipment must be worn. See the MSDS and local regulations for each material used.

The analyst is expected to be familiar with general laboratory practices, the technique of ICP-OES, and the equipment being used.

Preparation of Standards

Due to the linear response of the ICP, single point standards are used.

Prepare four stock standard solutions at the 50-µg/mL level, labeled as Stock Standards 2 through 5.

- This labeling follows SPEX numbering convention, wherein standard number 1 is used for rare earth elements, which are not addressed in this method.

- Four different calibration standards are prepared to ensure solubility and minimize spectral overlap interferences.
1. Label each of four 500-mL polypropylene volumetric flasks as Stock Standard, the number (2 through 5), 50 µg/mL, and list the elements in the solution, see Table 2.
 2. Pipet 25 mL of the commercial 1000 µg/mL standard solutions of the elements listed in Table 2 into their respective volumetric flasks.

Table 2
Elements Contained in the Stock Standard Solutions

<u>Std. 2</u>	<u>Std. 3</u>	<u>Std. 4</u>	<u>Std. 5</u>
Aluminum (Al)	Tin (Sn)	Molybdenum (Mo)	Potassium (K)
Cadmium (Cd)		Titanium (Ti)	Sodium (Na)
Calcium (Ca)		Zirconium (Zr)	Strontium (Sr)
Chromium (Cr)			
Cobalt (Co)			
Copper (Cu)			
Iron (Fe)			
Lead (Pb)			
Magnesium (Mg)			
Manganese (Mn)			
Nickel (Ni)			
Vanadium (V)			
Zinc (Zn)			

3. Dilute to mark with water and mix well.
4. Label an additional 500-mL polypropylene volumetric flask as Scandium Stock Standard, 100 µg/mL.
5. Pipet 50 mL of the commercial 1000 µg/mL scandium standard solution into the labeled 500-mL polypropylene volumetric flask.
6. Dilute to mark with water and mix well.

Prepare the five Calibration Standard Solutions as follows:

1. Label each of four 100-mL polypropylene volumetric flasks as Calibration Standard, the number (2 through 5), 10 µg/mL, and list the elements in the solution. Label a fifth 100-mL polypropylene volumetric flask as Calibration Blank.
2. Pipet 20 mL of the four Stock Standard Solutions into their respective 100-mL polypropylene volumetric flasks.
3. Pipet 5 mL of concentrated sulfuric acid into each of the five volumetric flasks.
4. Pipet 5 mL of the 100 µg/mL Scandium Stock Standard into each of the five flasks.
5. Dilute to mark with water and mix well.
 - The Calibration Standard Solutions contain 10 µg/mL of the elements and 5 µg/mL of scandium stock (internal) standard, in 5% of sulfuric acid to match the matrix of the samples.

Preparation of Spectrometer

Start up the ICP-OES, ignite the plasma according to the manufacturer's recommendations, and allow a minimum of 30 minutes before starting the analysis. When recommended by the manufacturer, perform a wavelength calibration prior to the start of the analysis. Aspirate the standards and blank to establish response factors prior to aspiration of the samples. Table 3 lists recommended wavelengths to be used for the analyses.

Table 3
Recommended Wavelengths

<u>Element</u>	<u>λ, nm</u>	<u>Element</u>	<u>λ, nm</u>
Aluminum	396.152	Manganese	257.610
Cadmium	214.438	Molybdenum	202.030
Calcium (high level)	422.673	Nickel	231.604
Calcium (low level)	393.366	Potassium	766.490
Chromium	206.149	Scandium	424.683
Cobalt	238.892	Sodium	589.592
Copper	324.754	Strontium	460.739
Iron (high level)	273.955	Tin	189.989
Iron (low level)	238.204	Titanium	323.452
Lead	220.353	Vanadium	292.402
Magnesium (high level)	279.079	Zinc	206.200
Magnesium (low level)	279.553	Zirconium	343.823

Sample Preparation

Samples are analyzed on an as received (AR) basis unless otherwise specified. However, for samples containing large amounts of carbon and/or organics the samples may be analyzed on a volatile free (VF) basis. If a sample is to be analyzed volatile free, weigh portions of the sample for this test and for LOI at 500°C at the same time. Analyze the LOI aliquot by UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents." Samples that are wet with water are dried overnight at 105°C.

Sample homogeneity is critical to obtain reproducible results. For samples containing or composed of large, heterogeneous particles, pulverize the sample in a mixer mill to a consistency of approximately 80 mesh or finer. In cases where only a small amount of sample is available, use a mortar and pestle or alternative grinder vessels.

1. Weigh, to the nearest 0.1 mg, approximately 0.4 g of sample into a tared 250-mL Teflon beaker.
 - For convenience, dry, free-flowing samples may be weighed using a weighing scoop, and then transferred into the beaker.
2. Add 10 mL of water and 10 mL of concentrated sulfuric acid to the beaker. Slowly add 10 mL of concentrated hydrofluoric acid from a polypropylene graduated cylinder, swirl to mix the contents of the beaker.
3. Place the uncovered beaker on a 150°C hot plate. Heat until white fumes of sulfuric acid appear. Remove the beaker from the hot plate and allow it to cool.

4. If the solution in the beaker is black or dark brown, or if it contains particulate matter, it may contain organics and/or carbon. Decompose by adding a few drops of concentrated nitric acid and heating on the hot plate until white fumes of sulfuric acid begin to evolve. Remove the beaker from the hot plate and allow it to cool.
5. If the solution in the beaker contains no particulate matter, proceed to the next step. If any particulates remain, add approximately 20 mL of concentrated hydrochloric acid and 1 mL of nitric acid using graduated cylinders, cover with a Teflon watch glass and return the beaker to the hot plate. Boil gently until the solution is clear. Remove the beaker from the hot plate and allow it to cool. See Note 2.
6. Quantitatively transfer the contents of the beaker to a 200-mL polypropylene volumetric flask, rinsing the beaker and watch glass several times with water.
7. Using the Rainin pipet, add the appropriate amount of scandium standard for desired level of standard, typically 10 mL for 5 ppm.
8. Dilute to the mark with water and mix well.

The prepared sample solutions are appropriate for the determination of minor and trace concentrations of elements in the sample. To determine major (matrix) elements in the sample, a further 20:1 dilution is necessary.

1. Pipet 10 mL of the prepared sample solution into a 200-mL polypropylene volumetric flask.
2. To restore the acid matrix, add 9.5 (or 10) mL of concentrated sulfuric acid.
3. To restore the internal standard level, using a Rainin pipet, add 9.5 mL of the Scandium Stock Standard.
4. Dilute to mark with water and mix well.

Sample Analysis

Follow the spectrometric procedure as described under *Preparation of Spectrophotometer*. Following aspiration of the standards and blank, and instrument calibration, enter the appropriate weight per volume for the sample into the data system, and aspirate the samples. The data system will calculate the mass-% metal in the sample after pretreatment, as described in *Sample Preparation*, and print the result.

Calculations

If the results are to be reported as received, disregard Equation 1 and continue to the next paragraph. If the results are to be reported on a volatile free basis, correct the mass of sample used as shown in Equation 1.

$$W = \frac{M(100 - L)}{100} \quad (1)$$

where:

L = LOI from UOP Method 954, mass-%
M = mass of sample as received, g
W = mass of sample used in calculation
100 = percent

The calculations are normally performed by the data system after the analyst enters the appropriate values for weights and dilution volumes.

Report results to the nearest 0.01 mass-%, but no greater than three significant figures. Also report whether the sample was analyzed as received (AR) or volatile free (VF).

Notes

1. Silicon cannot be determined by this method because silicon dioxide is insoluble in the acids used. Any silicon present is removed by boiling with hydrofluoric acid to avoid the necessity of filtering the sample. If the concentration of silicon is desired, an alternative sample preparation technique, such as lithium tetraborate fusion, not described herein, may be used.
2. Barium cannot be determined by this method because barium forms an insoluble sulfate with sulfuric acid. If barium is present, the precipitate formed can be removed by filtering or centrifuging the solution. If the determination of barium is desired an alternative sample preparation technique without using sulfuric acid, not described herein, may be used.
3. The selected emission lines reflect the most common unknown sample matrices and elemental concentrations. If the samples have an unusual matrix, major elements such as Ni, V, Cr, rare earths or others, the analyst is to check for spectral interferences due to emission line overlaps. If interferences are detected, different line selections are to be made.

Precision

Based on 6 replicate determinations, the estimated standard deviation (esd) was calculated for the metals listed in Table 4. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table 4 with 95% confidence.

Table 4
Repeatability, mass-%

<u>Metal</u>	<u>Concentration</u>	<u>esd</u>	<u>Allowable Difference</u>
Aluminum	3.2	0.03	0.12
Calcium	3.1	0.04	0.14
Chromium	1.8	0.02	0.06
Cobalt*	0.03	0.005	0.02
Copper	0.01	0.0009	0.01
Iron	41.0	0.3	1.1
Manganese	0.8	0.02	0.05
Magnesium	0.9	0.02	0.08
Nickel	1.8	0.03	0.10
Sodium	1.0	0.02	0.08
Titanium	1.0	0.01	0.05
Vanadium	0.5	0.005	0.02
Zinc	0.1	0.0004	0.01

* Near the detection limit.

It is expected that all elements will have similar precision above 0.1 mass-%. Precision for levels below 0.1 mass-% can vary depending on the detection limit for the specific element.

The data in Table 4 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 3 hours. The labor requirement for one analysis is 2.5 hours, or in groups of five or more samples, 2 hours.

Suggested Suppliers

Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850)
www.sigma-aldrich.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

PerkinElmer Analytical Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794
(203-925-4600) www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

Rainin Instrument Co., Mack Road, Woburn, MA 01801 (800-472-4646) www.rainin.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

Appendix

Microwave Digestion of Catalyst

Scope

This appendix describes an alternative catalyst digestion procedure using a microwave-based heating technique. Any carbon present on the sample must be removed prior to microwave digestion.

Outline of Method

The sample, after removal of carbon if necessary, is weighed into a Teflon vessel and diluted with a mixed acid solution. The vessel is placed in a specially configured microwave oven and heated for several minutes. The digest is then analyzed as described in the body of the method. Silicon can be analyzed using this digestion method.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following apparatus are an addition or substitution to that listed in the body of the method:

Bottle, 2-L, Nalgene Polypropylene with polypropylene screw closure. Fisher Scientific, Cat No 02-924A

Cylinders, graduated, Class B, 10-, 50-, 500-, and 1000-mL, Fisher Scientific, Cat. Nos. 08-552-4H, -4B, -4E, and -4F, respectively

Microwave, 1200 Watt, CEM, Model MARS 5 or Xpress, including all vessels and accessories specific to the particular instrument. (A lower wattage instrument is acceptable; times for digestion must be determined)

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following reagents and materials are an addition or substitution to those listed in the body of the method:

ICP Mixed Acid. Using graduated cylinders, measure 720 mL of de-ionized water, 480 mL of H_3PO_4 , 400 mL of HCl , and 20 mL of HNO_3 into a 2-L polypropylene bottle. Mix thoroughly and allow to cool.

Phosphoric acid, 85%, Certified ACS, Fisher Scientific, Cat. No. A-242-1

Silicon solution, aqueous, 1000 $\mu\text{g/mL}$, SPEX Industries, Inc., Cat. No. PLSI9-2X

Preparation of Standards

If the analysis of silicon is desired, silicon can be added to Stock Standard #4. Follow the same procedure as outlined in the main body of the method and label accordingly. Concentrations of 0.01 to 2.5% are read on the ICP at 251.611 λ , nm.

In preparing the final calibration standard solution, eliminate the 5 mL addition of sulfuric acid. Instead, pipet 20 mL of ICP Mixed Acid and 2 mL of hydrofluoric acid. In the closed system of the microwave vessels, none of the acid matrix will be eliminated during the digestion process.

Procedure

The analyst is expected to be familiar with the technique of microwave digestion and with the equipment being used.

Follow the main body procedure for volatile free analysis and removal of carbon. Carbon must be removed before digestion in the microwave vessels.

1. Weigh approximately 0.4 g of the as-received catalyst or catalyst support to the nearest 0.1 mg into the Teflon microwave digestion vessel. If results are to be reported on a volatile-free basis, weigh out a separate portion of the sample for the determination of LOI as directed in UOP Method 954.
 - Some microwave digestion vessels use an optional glass liner. If a glass liner is used, the sample cannot be analyzed for silicon.
2. Using a graduated cylinder, slowly add 40 mL of ICP mixed acid to the digestion vessel. If highly reactive metals are present, allow the reactivity to subside before continuing. This will be observed easily in the vessel.
3. Using a polypropylene graduated cylinder, add 2 mL of HF to each vessel.
4. Repeat the above procedure for each sample to be analyzed. If the system uses a control vessel, treat this as a sample. The contents of the control vessel are generally discarded after digestion, but can be used for blank analysis if cleanliness of the digestion vessel is certain.
5. Cap and seal the digestion vessels according to manufacturer's instructions and place in the microwave oven using the appropriate carousel.
6. If pressure and/or temperature probes are required, make sure they are properly applied and that a control vessel that matches the sample vessels is used.

Follow manufacturer recommendations for operation of the microwave digestion system. Use Table A1 as a guide for the digestion method.

Table A1
Operating Conditions

<u>Number of Samples*</u>	<u>Variable power, W</u>	<u>Ramp time, minutes</u>	<u>Temp, °C</u>	<u>Pressure, psi</u>	<u>Time at temp, minutes</u>
1 - 15	1200	25	180	150	10
16 - 25	1200	35	180	150	10
26 - 40	1200	45	180	150	10

*The maximum number of samples that can be digested at one time depends upon the equipment being used.

7. Allow vessels to cool to near ambient temperature before removing them from the oven.
8. Open the vessels.
9. Carefully rinse the seal and the inside of the cap with water, catching the rinsings in the vessel.
10. Quantitatively transfer the solution with water into a 200-mL polypropylene volumetric flask.

11. Using a pipet, add 5 mL of 100 µg/mL Scandium Stock Standard solution to the volumetric flask. Fill to the mark with water; cap and mix by inverting several times.
12. Analyze the digest as described in the body of the method.

Notes

1. Table A is based upon a variable power, 1200 watt system. A lower wattage system can be used with adequate adjustments to ramp times.
2. If running a MARS Xpress system, extreme caution should be exercised for samples of unknown content as the pressure is not known or monitored.
3. Be sure the temperature and pressure limits of the system and vessels are known and followed.

Precision

Based on 52 replicate determinations on a control standard over a period of 12 months, the estimated standard deviation (esd) was calculated for the metal listed in Table A2. Two tests performed by different analysts on different days should not differ by more than the intermediate precision allowable difference shown in Table A2 with 95% confidence.

Table A2
Intermediate Precision, mass-%

<u>Metal</u>	<u>Concentration</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Nickel	0.98	0.020	0.04

Time for Analysis

The elapsed time for an analysis is 1.5 to 2.0 hours, depending upon the number of samples being digested in the microwave. The labor requirement is 1.0 hour for one sample; less if multiple samples are being analyzed.

Suggested Supplier

The following supplier is an addition or substitution to that listed in the body of the method:

CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200 (704-821-7015) www.cem.com