



Impurities in Catalysts by ICP-OES

UOP Method 303-19

Scope

This method is for determining trace metals in fresh, regenerated and spent alumina-, silica-, or aluminosilicate- (silica/alumina-) based catalysts by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Ordinarily, the metals determined include calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), silicon (Si), sodium (Na), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Silicon is not determined when it is a component of the catalyst base. Arsenic (As) and phosphorous (P) can be determined but are not ordinarily present on fresh catalysts. They may, however, be present on regenerated or spent catalyst. Barium (Ba) and mercury (Hg) cannot be determined because barium sulfate precipitates and mercury volatilizes. Barium can be determined using the fusion technique described in UOP Method 926, "Silicon and Aluminum in Fresh Catalysts by Lithium Tetraborate Fusion/ ICP-OES." Other elements also can be determined, if required. The specified elements can be determined within the concentration ranges listed in Table 1. Typical concentration ranges are 0.005-1.0 mass-%.

Table 1
Applicable Concentration Ranges, mass-%

Element	Concentration Range on Catalyst	Element	Concentration Range on Catalyst
As	0.020-1.0	Na	0.005-2.0
Ca	0.001-2.0	Ni	0.005-1.0
Co	0.005-2.0	P	0.010-1.0
Cr	0.005-1.0	Pb	0.010-1.0
Cu	0.001-0.50	Si*	0.005-0.20
Fe	0.005-2.0	Sn	0.010-1.0
K	0.050-3.0	Ti	0.005-2.0
Mg	0.001-0.50	V	0.003-1.0
Mn	0.001-0.50	Zn	0.005-0.50
Mo	0.005-1.0		

**See Note 1*

This method is not applicable to noble metals and modifiers on catalysts.

This method cannot be used for determining metals in alpha-alumina based catalyst because alpha-alumina is not solubilized under the conditions of this procedure.

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 THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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An alternative microwave-based dissolution technique is described in the *Appendix*.

References

ASTM Method D1193, "Specification for Reagent Water," www.astm.org

ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis," www.astm.org

UOP Method 926, "Silicon and Aluminum in Fresh Catalysts by Lithium Tetraborate Fusion/ ICP-OES," www.astm.org

UOP Method 954, "Loss on Ignition (LOI) 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 catalyst samples are decomposed by digestion in acids. Hydrofluoric acid is used to remove silica from silica- or silica/alumina-based catalyst digests by volatilization. Scandium is added to the digests as an internal standard. The sample solutions are then analyzed by ICP-OES with appropriate, matrix-matched standards.

Apparatus

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

Balance, readability 0.0001 g

Beaker, Teflon™ PTFE, 250-mL, Fisher Scientific, Cat. No. 02-586-1H

Bottle, wash, for water, 500-mL, VWR, Cat. No. 16651-904

Bottletop Dispensers, Analog-Adjustable, 2.5 to 25mL, Dispensette S, with Recirculation Valve, Fisher Scientific, Cat No. 50-153-1859, 2 required

- Not hydrofluoric acid compatible

Bottletop Dispenser, Analog-Adjustable, 1 to 10 mL Dispensette S Trace Analysis, with platinum-iridium valve springs, Fisher Scientific, Cat. No. # 13-689-058

- To use for concentrated hydrofluoric acid

Cylinders, graduated, polypropylene, 10- and 50- mL, Fisher Scientific, Cat. Nos. 08-572A and -572C, respectively

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

Hot plate, variable heat to at least 300°C, Fisher Scientific, Cat. No. HP88850100

Inductively Coupled Plasma-Optical Emission Spectrometer, computer controlled, having a bandpass of 0.010 nm (FWHM) or better. The instrument must have the ability to use internal standards, perform background corrections, and must measure the internal standard response concurrently with each element response. A Perkin-Elmer Optima 8300 spectrometer with an HF resistant sample introduction system, or its equivalent, is required

Pipets, Sartorius™ Biohit™ eLINE™ Single-Channel Electronic Pipet, total volume, 0.5 to 5-mL, Fisher Scientific Cat. No. 14-559-375

- Periodically, check the pipette accuracy by weighing out deionized water before preparing the stock solutions.

Pipet tips, Eppendorf epTips, 0.1 to 5 -mL, and 0.5 to 10 –mL Fisher Scientific Cat. No. 05-403-29, 05-403-116, respectively

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580, Part No. SEQ3126ACGA

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580, Part No. SEQ3126ACGA

Watch glass, Teflon PTFE, 100-mm diameter, Fisher Scientific, Cat. No. 02-617-1E

Reagents and Materials

References to catalogue 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, Certified ACS Plus, VWR, Cat. No. BDH3030

Hydrofluoric acid, concentrated, trace metals grade, Fisher Scientific, Cat. No. MK264018

Hydrogen peroxide, 30%, Certified ACS, Fisher Scientific, Cat. No. H325-500

Nitric acid, concentrated, Certified ACS Plus, Fisher Scientific, Cat. No. A200-212

Nitrogen or Argon, 99.99% minimum purity, water/oil free, ICP optics purge gas

Single element standard, Aluminum (Al), 10,000 µg/mL, SPEX Industries, Inc., Cat. No. PLAL1-3X, used for matrix matching

Single element standard, Potassium (K), 10,000 µg/mL, SPEX Industries, Inc., Cat. No. PLK1-3X

Scandium metal solution, aqueous, 10,000 µg/mL, SPEX CertiPrep, Inc., Cat. No. PLSC2-3X, for use as an internal standard

Scandium internal standard, aqueous, 500-µg/mL. To prepare 500 µg/mL, pipet 5 mL of the 10,000-µg/mL scandium metal solution into a 100-mL volumetric flask. Fill to the mark with deionized water. Cap and invert several times to mix. Store in a 125-mL polypropylene bottle. The solution should remain stable for two months

Single element standards, 1000 µg/mL each, As, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, and Zn, SPEX Industries, Inc., Cat. Nos. PLAS2-2X, PLCA1-2X, PLCO2-2X, PLCR1-2X, PLCU2-2X, PLFE2-2X, PLMG2-2X, PLMN2-2X, PLMO9-2X, PLNA2-2X, PLNI2-2X, PLP9-2X, PLPB2-2X, PLSI9-2X, PLSN5-2X, PLTI9-2X, PLV2-2X, and PLZN2-2X, respectively

Sulfuric acid, concentrated, Certified ACS Plus, Fisher Scientific, Cat. No. A300SI 212

Water, ASTM D1193 Type I reagent grade water exact

Procedure

Caution: All subsequent steps involving additions of acids and heating of samples and digests must be performed in a properly operating fume hood, using appropriate precautions. Gloves, safety glasses,

goggles, and/or face shield, and other appropriate personal protective equipment must be worn. See the safety data sheet (SDS) 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

To ensure accurate blending, use the techniques described in ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards." It has been found convenient to use electronic pipets for the preparation of the Stock Solutions. A few Single Element Standards contain a trace amount of HF and will be so labeled.

If the microwave digestion procedure as described in the *Appendix* is to be used in place of the sample preparation described on Page 5, adjust the acid matrix in the Calibration Standards to fit the acids used in the microwave dissolution.

Prepare internal standard stock solution., 100- $\mu\text{g/mL}$:

To prepare 100 mL, pipet 1 mL from a 10,000- $\mu\text{g/mL}$ scandium (Sc) metal solution into a 100-mL volumetric flask. Fill to the mark with deionized water. Cap and invert several times to mix. Store in a 125-mL polypropylene bottle. The solution should remain stable for two months.

Prepare three Stock Solutions from the Single Element Standards as follows:

1. Clean three 500- mL polypropylene volumetric flasks and label them stock standard 1-3.
2. In the volumetric flasks labeled standards 1 and 3, pipet 25 mL of the Single Element Standards, distributed as shown in Table 2.
3. In the volumetric flask labeled standard 2 pipet 25 mL of the 1000- $\mu\text{g/mL}$ single element standards for Sn and Na as well as 12.5 mL of the 10,000- $\mu\text{g/mL}$ K standard.
 - Three different Stock Solutions are required to prevent solubility and spectral interference problems.

Table 2

Elements Contained in the Stock Standard Solutions

<u>Std. 1</u>	<u>Std. 2</u>	<u>Std. 3</u>
Arsenic (As)	Tin (Sn)	Molybdenum (Mo)
Calcium (Ca)	Sodium (Na)	Phosphorous (P)
Chromium (Cr)	Potassium (K)	Silicon (Si)
Cobalt (Co)		Titanium (Ti)
Copper (Cu)		
Iron (Fe)		
Magnesium (Mg)		
Manganese (Mn)		
Nickel (Ni)		
Lead (Pb)		
Vanadium (V)		
Zinc (Zn)		

4. Dispense 5 mL of nitric acid to each flask. Fill to the mark with water. Cap and mix by inverting several times.
 - Bottle top dispensers are used for safety and efficiency purposes to dispense concentrated acids. If compatible bottletop dispensers are unavailable, then compatible graduated cylinders suffice.

5. Label the flask as containing 50 µg/mL of each of the elements, except for standard #2, label as 250 µg/mL K. Stock Solutions are typically stable for six months.

ICP Calibration Standard solutions are prepared by diluting the Stock Solutions. In addition, a solution containing aluminum is added to match the Calibration Standard matrix with the sample matrix.

Prepare three Calibration Standards from the Stock Solutions as follows:

1. Into each of the three 100-mL polypropylene volumetric flasks, dispense 20 mL of the respective Stock Solutions. Use a fourth 100-mL polypropylene volumetric flask as a blank.
2. If the samples to be analyzed are alumina-based catalysts, pipet 25-mL of the 10,000 µg/mL Aluminum Single Element Standard to each of the four volumetric flasks. If the samples are silica/alumina or silica-based, add correspondingly less Aluminum Single Element Standard. If the samples are silica-based, add no Aluminum Single Element Standard.
 - For many samples, the alumina concentration is known and can be matrix matched. If the alumina concentration is unknown, analyze the sample digest by preparing a Calibration Standard solution of 1000-µg/mL Al, 1-µg/mL Sc, the acids as described herein, and by analyzing the digest against this Working Standard.
 - To deliver 25 mL to the volumetric flask using the specified 5-mL pipet will require pipetting five, 5-mL aliquots successively.
3. Slowly dispense 5 mL of sulfuric acid and 10 mL of hydrochloric acid to the volumetric flasks.
4. Using a pipet, add 1 mL of 100 µg/mL Sc Single Element Standard solution to the flasks. Fill to the mark with water. Cap and mix by inverting several times.
5. Label the volumetric flasks as containing 10 µg/mL of each of the elements added with standard 2 having 50 µg/mL K, 1 µg/mL Sc, and indicate the concentration of Al. Calibration Standards should be discarded after one month.

Since the response of the ICP-OES is linear within the defined range of quantitation, single point standards are used.

Preparation of Spectrometer

Start up the instrument and ignite the plasma according to the manufacturer's recommendations. For instruments that have both axial and radial view options, use the axial view. Wait a minimum of 30 minutes after the plasma is ignited for the instrument to stabilize. When recommended by the manufacturer, perform a wavelength calibration prior to the start of the analysis. Aspirate the Calibration Standard solutions and the reagent blank. Table 3 lists recommended wavelengths to be used for the analyses.

Calibration

Establish the elemental responses compared to scandium. These calculations are performed by the data system after the analyst enters the appropriate values for weights and dilution volumes.

Sample Preparation

The number of steps required to prepare samples for analysis depends on whether silica is a constituent, whether organic compounds or carbon are present, and if the catalyst contains platinum group metals. See *Notes*. Samples are analyzed on an as received (AR) basis unless otherwise specified. If a sample is to be analyzed on a volatile free (VF) basis, weigh portions of the sample both for this test and for LOI 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."

Table 3**Recommended Wavelengths**

<u>Element</u>	<u>λ, nm</u>	<u>Element</u>	<u>λ, nm</u>	<u>Element</u>	<u>λ, nm</u>
As	188.979	K	766.491	Pb	220.353
Ca ($\leq 0.1\%$)*	393.366	Mg	285.213	Si	288.158
Ca ($\geq 0.1\%$)*	422.673	Mn	257.610	Sn	189.989
Co	228.616	Mo	202.030	Ti	334.941
Cr	206.149	Na	589.592	V	292.402
Cu	324.754	Ni	231.604	Zn	206.191
Fe	238.204	P	178.221		

***Different wavelengths are used for calcium, depending upon its concentration. Calibrate at both wavelengths**

Prepare samples per the following procedure. An alternative microwave-based dissolution technique is described in the *Appendix*.

1. Samples are not typically ground because of the risk of contamination from the grinding equipment. However, grinding the sample will homogenize the sample and reduce the dissolution time. If the sample is to be ground, grind it in a mixing mill to a consistency of approximately 80 mesh or finer.
2. Weigh, to the nearest 0.1 mg, approximately 1.0 g of sample into a tared 250-mL Teflon beaker. Add 20 mL of water and dispense 10 mL of concentrated sulfuric acid to the beaker. If the sample does not contain silica, proceed to Step 4.
 - Silica is not significantly soluble in sulfuric acid; therefore, do not report any Si concentrations greater than 10 $\mu\text{g/mL}$ in the digest, or 0.2 mass-% in the solid catalyst. If the concentration of Si at higher levels is important, analyze the sample by UOP Method 926, "Silicon and Aluminum in Fresh Catalysts by Lithium Tetraborate Fusion/ICP-AES."
3. If the sample contains silica, slowly dispense 4 mL hydrofluoric acid into the beaker.
 - CAUTION: Hydrofluoric acid is a hazardous material to handle. It can cause severe burns, which, under certain circumstances, can be fatal. Specialized first aid procedures are required for treatment of HF burns. Consult the hydrofluoric acid SDS for further information.
 - If using graduated cylinder, polypropylene should be used to ensure compatibility with hydrofluoric acid.
4. Mix the contents of the beaker by swirling and place the uncovered beaker on a hot plate set at about 250°C until white fumes of sulfuric acid begin to evolve. Remove the beaker from the hot plate and allow it to cool. If the digest is clear and uncolored, proceed to Step 7.
 - A dark-colored digest indicates the presence of organics, carbon, or platinum group metals (see Note 2).
 - To remove the organics and carbon, cover with a Teflon™ watch glass, and slowly add a few drops of concentrated nitric acid to the digest.
5. Uncover the beaker, then place the beaker on a hot plate until white fumes begin to evolve. Remove the beaker from the hot plate and allow it to cool. If the digest is clear and uncolored, proceed to Step 7.
6. If the digest remains dark-colored after the nitric acid treatment, reduced platinum group metals are present. Allow the solution to cool, then add 10 mL of concentrated hydrochloric acid and 2-3 drops of hydrogen peroxide to the beaker. Cover with a Teflon watch glass and return the beaker to the hot plate. Boil gently until the solution is clear. Remove the covered beaker from the hot plate and allow it to cool.
7. Add approximately 40 mL of water to the beaker. Add 20 mL of concentrated hydrochloric acid to the beaker. If 10 mL of concentrated hydrochloric acid was added in Step 6, only add an additional 10 mL of concentrated hydrochloric acid at this point. Cover the beaker with a Teflon

watch glass and return it to the hot plate. Boil gently until the aluminum sulfate crystals are dissolved. If a white precipitate is present, see Note 3.

8. Quantitatively transfer the contents of the beaker to a 200-mL polypropylene volumetric flask, rinsing the beaker and watch glass several times with water.
9. Using a pipet, add 2 mL of 100 µg/mL Sc Single Element Standard solution to the volumetric flask. Fill to the mark with water; cap and mix by inverting several times.

Sample Analysis

Follow the procedure as described under *Preparation of Spectrometer*. Aspirate the standards and blank, enter the appropriate weights and volumes in the instrument, and aspirate the sample digests.

Calculations

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

If the results are to be reported as received, disregard Equation 1. If the results are to be reported on a volatile free (VF) basis, correct the mass of sample used as shown in Equation 1 and enter the VF weight into the data system.

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

where:

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

Report results to the nearest 0.001 mass-%. Also report whether the sample was analyzed as received (AR) or volatile free (VF).

Notes

1. The maximum solubility for silicon in the acid matrix used in this method is approximately 60 µg/mL in solution, or 1.2 mass-% on the catalyst. The upper concentration limit for silicon by this method has been placed at 10 µg/mL in solution, or 0.2 mass-% on the catalyst. If silicon determination above this level is required, use UOP Method 926, "Silicon and Aluminum in Fresh Catalysts by Lithium Tetraborate Fusion/ICP-OES."
2. Samples containing more than 10% carbon should be ignited to remove carbon before digestion. Analysis of samples with higher carbon levels will lead to erroneous results due to mismatched aluminum levels between the samples and standards. Use the procedures in UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," at 550°C for one hour. Samples that are ignited may lose volatile elements such as arsenic and phosphorus.
3. Barium cannot be determined by this method because the barium sulfate formed during sample digestion is insoluble in the acids used. If barium is present, an insoluble precipitate will form. A trace of precipitate will settle to the bottom of the containers and not interfere with the analysis. If significant quantities of precipitate are formed, the sample cannot be analyzed by this method. If barium determination is necessary, a fusion technique like that described in UOP Method 926, "Silicon and Aluminum in Fresh Catalysts by Lithium Tetraborate Fusion/ ICP-OES." Mercury cannot be determined because it is volatilized during sample preparation.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Intermediate Precision

A nested design was carried out for hot digestion trace metals ICP analysis by two analysts in one laboratory, with each analyst performing two analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and Intermediate Precision, mass-%

Component	Mean	Repeatability		Site Precision	
		Within Day esd	Allowable Difference	Within Lab esd	Allowable Difference
As	0.020	0.0003	0.001	0.0003	0.001
Ca	0.021	0.0003	0.001	0.0013	0.006
Co	0.020	0.0001	0.001	0.0007	0.004
Cr	0.020	0.0003	0.001	0.0003	0.001
Cu	0.019	0.0003	0.001	0.0005	0.002
Fe	0.038	0.0001	0.001	0.0013	0.008
K	0.107	0.0025	0.010	0.0040	0.016
Mg	0.019	0.0003	0.001	0.0005	0.002
Mn	0.021	0.0003	0.001	0.0004	0.002
Mo	0.020	0.0003	0.001	0.0004	0.002
Na	0.019	0.0001	0.001	0.0003	0.002
Ni	0.020	0.0001	0.001	0.0002	0.001
P	0.020	0.0005	0.002	0.0007	0.003
Pb	0.019	0.0001	0.001	0.0006	0.004
Si	0.025	0.0033	0.013	0.0053	0.032
Sn	0.311	0.0029	0.012	0.0069	0.031
Ti	0.021	0.0003	0.001	0.0003	0.001
V	0.020	0.0003	0.001	0.0006	0.004
Zn	0.023	0.0001	0.001	0.0003	0.002

The data in Table 4 represent short term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of 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 4 hours. The labor requirement for one analysis is 2 hours, or in groups of 5 or more samples, 1.8 hours.

Suggested Suppliers

Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300) www.fishersci.com

Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg, NJ 08865 (908-859-2151)
www.jtbaker.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-648-4000)
www.mathesontrigas.com

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

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.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. It is specific for carbon free samples.

Outline of Method

The sample is weighed into a Teflon vessel (or quartz vessel if the silica is below 10 µg/mL) and diluted with a mixed acid solution. The vessel is placed in a specially configured microwave oven and heated for several minutes. The sample solution is then analyzed as described in the body of the method.

Apparatus

If microwave heating is used, the hot plate and other miscellaneous equipment listed under *Apparatus* in the body of the method are not required.

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

The following apparatus is 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, 10-, 50-, 500-, and 1000-mL, Fisher Scientific, Cat. Nos. 08-552-4H, -4B, -4E, and -4F, respectively

Microwave, UltraWAVE, 1500-Watt, Milestone, or equivalent, including all vessels and accessories specific to the instrument model. (A lower wattage instrument is acceptable; times for digestion must be determined)

Teflon™ Vial, 40mL, Milestone, Cat. No. HB00077

Teflon™ cap, 25mm, Milestone, Cat. No. DD0130

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 790 mL of de-ionized water, 50 mL of concentrated H₂SO₄ and mix thoroughly, allow to cool. Add 120 mL of concentrated HCl, and slowly add 40 mL of concentrated HNO₃ into a 2-L polypropylene bottle. Mix thoroughly, allow to cool.

Procedure

Preparation of Standards

Follow the procedure as described in the body of the method but change the acid matrix in the Calibration Standards and internal standard to fit the acids used in the microwave dissolution.

Sample Preparation

The analyst is expected to be familiar with the technique of microwave digestion and with the equipment being used. This portion of the procedure is written based upon the use of an UltraWAVE microwave. If a different microwave is used, modify the procedure as necessary.

1. Weigh approximately 0.25 g of the as received catalyst or catalyst support to the nearest 0.1 mg into Teflon or quartz 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.
2. Using a graduated cylinder, add 15 mL of ICP mixed acid to the Teflon™ vial.
3. If silicon is a possible contaminant, dispense 2 mL of HF. If silicon is a component of the base, add 4 mL of HF.
4. Cap the digestion vessels and place in the microwave oven using the appropriate carousel.
5. Follow manufacturer recommendations for operation of the microwave digestion system. For gamma alumina and silica/alumina materials follow the guidelines in Table A1. For theta alumina base material, run the microwave using conditions in Table A1 twice.

Table A1
Operating Conditions for Gamma Alumina and Silica/Alumina Materials

<u>Ramp time (min)</u>	<u>Temp 1 (°C)</u>	<u>Pressure (bar)</u>	<u>Temp 2 (°C)</u>
40	245	150.0	60
20	245	150.0	60

6. Allow vessels to cool to near ambient temperature before removing them.
7. Open the vessels.
8. Carefully rinse the inside of the cap with water, catching the rinsings in the vessel.
9. Rinse the Teflon vessels with 5mL of hydrochloric acid.
10. Quantitatively transfer the solution with water into a 50-mL polypropylene volumetric flask.
11. Using a pipet, add 1 mL of 100 µg/mL Sc Single Element 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.

Precision

A nested design was carried out for microwave digestion trace metals ICP analysis by two analysts in one laboratory, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table A2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table A2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable differences shown in Table A2 with 95% confidence.

Table A2
Intermediate Precision, mass-%

Component	Mean	Repeatability		Site Precision	
		Within Day esd	Allowable Difference	Within Lab esd	Allowable Difference
As	0.020	0.0003	0.001	0.0004	0.002
Ca	0.021	0.0003	0.001	0.0003	0.001
Co	0.020	0.0003	0.001	0.0004	0.002
Cr	0.020	0.0001	0.001	0.0004	0.002
Cu	0.019	0.0003	0.001	0.0007	0.003
Fe	0.037	0.0006	0.002	0.0012	0.005
K	0.100	0.0003	0.001	0.0023	0.014
Mg	0.020	0.0003	0.001	0.0008	0.004
Mn	0.021	0.0003	0.001	0.0007	0.003
Mo	0.020	0.0001	0.001	0.0004	0.002
Na	0.018	0.0003	0.001	0.0004	0.002
Ni	0.020	0.0003	0.001	0.0004	0.002
P	0.020	0.0003	0.001	0.0009	0.006
Pb	0.020	0.0003	0.001	0.0007	0.004
Si	0.099	0.0049	0.019	0.0112	0.050
Sn	0.307	0.0022	0.009	0.0038	0.015
Ti	0.021	0.0003	0.001	0.0005	0.002
V	0.020	0.0003	0.001	0.0007	0.003
Zn	0.024	0.0003	0.001	0.0003	0.001

The data in Table A2 represent short term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of 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 an analysis is 1.5 to 3.0 hours. The labor requirement is 1.0 hour for one sample; less if multiple samples are being analyzed.