

TRACE METALLIC IMPURITIES IN FRESH CATALYSTS BY ICP-AES

UOP Method 927-92

SCOPE

This method is for determining trace levels of iron, sodium, calcium, magnesium, titanium, molybdenum and silicon in fresh alumina supported catalysts of known composition by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). All these elements except silicon can also be determined in fresh silica-alumina supported catalysts. The method is sufficiently flexible to permit the determination of other metals at trace levels if they can be brought into solution using the sample preparation procedure described. Concentration ranges covered are listed in Table 1. Catalysts containing *alpha*- or *theta*-alumina phases cannot be analyzed by this method.

OUTLINE OF METHOD

Alumina supported catalysts are dissolved using sulfuric acid, while silica-alumina supported catalysts are dissolved in sulfuric and hydrofluoric acids. The resulting sample solution is aspirated into an ICP-AES instrument and the concentration of each element is determined by comparison to matrix-matched standard solutions. Sample results are reported on an as-received basis.

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, 250-mL

Beaker, borosilicate glass, one-liter, used for warm water bath

Bottles, polypropylene, 125-mL and one-liter, Fisher Scientific, Cat. Nos. 02-925C and 925F, respectively

Cylinder, graduated, polypropylene, 10-, 25- and 50-mL

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Flasks, volumetric, polypropylene, 100-, 200- and 1000-mL

Funnel, disposable, 55-mm diameter, Fisher Scientific, Cat. No. 10-320A

Gloves, polyethylene

Hot plate, variable heat to at least 400°C

Inductively Coupled Plasma-Atomic Emission Spectrometer, computer controlled, having a bandpass of 0.010 nm (FWHM) or better, and covering the wavelength range specified in Table 1. The instrument must have the ability to use internal standards and perform background corrections, and must measure the internal standard response concurrently with each element response. A Perkin-Elmer Plasma 2000 spectrometer, or its equivalent, is required. A corrosion resistant sample introduction system is recommended.

Pipets, total volume, Class A, 5-, 10-, 15-, 20-, 25-, 30- and 50-mL, several of each required

Regulator, argon, two-stage, high purity, Matheson Gas Products, Model 3104-580

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3104-580

Thermometer, 0° to 100°C, for use with warm water bath, Fisher Scientific, Cat. No. 15-077C

Thermometer, electronic, with surface temperature probe, Omega Engineering, Cat. Nos. HH81 and 88108K, respectively

Watch glass, Teflon, 75-mm

Water purification system, to provide 18.3 megohm/cm, Type 1 Reagent Grade water, Fisher Scientific, Cat. No. 09-050-256

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean 18.3 megohm/cm, Type 1 Reagent Grade water.

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

Aluminum metal, shot, 99.9999% minimum purity, Johnson Matthey, Alfa Products, Cat. No. 10574

Argon, 99.995% minimum purity, ICP feed gas

Hydrochloric acid, concentrated, high purity, Baker Ultrex grade

Hydrofluoric acid, 48%

Hydrogen peroxide, 30%

Mercury metal, 99.99999% purity, SPEX Industries, Cat. No. HG05-50

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

Scandium solution, 1000-µg/mL, Inorganic Ventures, Cat. No. CGSC1-5

Standard solutions of metals, Fe, Na, Ca, Mg, Ti, Mo and Si solutions of 1000- $\mu\text{g/mL}$ concentrations, Inorganic Ventures, Cat. Nos. CGFE1-5, CGNA1-5, CGCA1-5, CGMG1-5, CGTI1-5, CGMO1-5 and CGSI1-5, respectively

Sulfuric acid, concentrated, high purity, Baker Ultrex Grade

Sulfuric acid, 80%. Mix four parts concentrated sulfuric acid with one part water, adding the acid to the water slowly to avoid spattering.

Yttrium solution, 1000- $\mu\text{g/mL}$, Inorganic Ventures, Cat, No. CGY1-5. Not required if the spectrometer specified in *APPARATUS* is used (see Note 1).

PROCEDURE

All subsequent steps involving handling and heating of concentrated acids or acid solutions must be performed in a fume hood.

Preparation of 10,000- $\mu\text{g/mL}$ Aluminum Solution

1. Weigh 10.0 ± 0.1 g of pure aluminum metal to the nearest 0.1 mg, and transfer to a one-liter polypropylene bottle.
2. Add one drop of mercury metal and 50 mL of concentrated high purity hydrochloric acid to the bottle.
3. Cap the bottle, but leave the cap loose to allow pressure release.
4. Place the bottle in a warm water bath (40 to 50°C) to start the reaction, and adjust the reaction rate to maintain an approximate 25-mm layer of bubbles (foam) above the liquid. If the layer exceeds this level, control by adding a little water to the bottle. As it decreases, add hydrochloric acid dropwise until a total of 100 mL (50 mL from Step 2 plus 50 mL additional) has been added. The dissolution takes several hours.
5. Transfer the solution to a one-liter polypropylene volumetric flask, quantitatively with water, using a funnel, after dissolution is complete.
 - The remaining mercury is also transferred to the bottle. After the aluminum solution has been consumed, dispose of the mercury by following appropriate statutory guidelines.
6. Cool to ambient temperature and dilute to volume. Cap and invert several times to mix thoroughly. Store in a one-liter polypropylene bottle.

Preparation of Calibration Standards

1. Prepare standards at the concentrations shown in Table 1 by appropriate dilution of the 1000- $\mu\text{g/mL}$ standard metal solutions, using the high purity hydrochloric acid. Silicon is not added to Standard 2 when determining impurities in silica-alumina supported catalysts.
 - Two standards are used for Ca to cover two different concentration ranges using two different wavelengths.
 - The standards are prepared in the same matrix as the samples, matching the acid and aluminum levels in the final sample dilution, see *Sample Preparation*.
 - If a spectrometer other than that specified in *APPARATUS* is used, yttrium can be substituted as the internal standard (see Note 1).

2. Prepare a calibration blank having the same matrix as the samples.
 - Due to the linear response of the ICP instrument, multiple standards are not required. A single standard and calibration blank are sufficient to define the calibration line slope and intercept for each element.

Table 1
Elements Sought, Recommended Wavelengths,
Concentration Ranges Covered and Recommended Standard Concentrations

Element	λ , nm	Concentration	Concentration, $\mu\text{g/mL}$	
		Range, mass-%	Std. 1	Std. 2
Fe	238.204	0.005 - 1.0	50.0	
Na	589.592	0.003 - 1.0	50.0	
Ca	393.366	0.001 - 0.10	5.0	
Ca	422.673	0.10 - 1.0		50.0
Mg	285.213	0.001 - 0.50	25.0	
Ti	323.452	0.002 - 1.0	50.0	
Mo	202.030	0.005 - 0.50	25.0	
Si*	252.611	0.005 - 0.20		10.0
Al	Matrix Element - Concentration to Match Sample			
Sc	Internal Standard (see Note 1)		50.0	50.0

*see Note 2

Sample Preparation

To avoid contamination, whole pill samples are dissolved in high purity acids, and plasticware is used throughout the preparation scheme. Use of gloves is also highly recommended. Clean labware must be used throughout this procedure. Previously cleaned beakers that are stored in drawers must be rinsed with dilute hydrochloric acid, followed by several rinses with water, just prior to starting the procedure below.

1. Weigh, to the nearest 0.1 mg, 1.0 g of whole pill catalyst into a 250-mL Teflon beaker.
 - Ground samples can be analyzed, but contamination from the grinding procedure is likely.
2. Add, with a polypropylene graduated cylinder, 25 mL of water to the beaker to wet the catalyst.
3. Add to the beaker, with a polypropylene graduated cylinder, 12 mL of 80% sulfuric acid, and swirl to mix the contents. If the catalyst support is alumina only, proceed to Step 5.
 - Add the acid slowly to avoid spattering.
4. Add to the beaker, with a polypropylene graduated cylinder, 10 mL of concentrated hydrofluoric acid, if the sample is a silica-alumina supported catalyst.
 - Appropriate safety precautions must be taken when handling hydrofluoric acid.
5. Place the beaker on a hot plate and adjust the heat to achieve mild boiling.
6. Cover the beaker with a Teflon watch glass, if the sample is alumina only (no HF added), and heat until the sample is completely dissolved, then proceed to Step 8.
7. Continue heating while slowly increasing the temperature until the evolution of thick white fumes characteristic of sulfuric acid, if the sample is silica-alumina.

- This will volatilize the silicon as the tetrafluoride and remove any residual HF.
 - The hot plate temperature must not exceed 300°C, as measured with a surface probe, or the Teflon beaker will deform and/or melt.
8. Remove the beaker from the hot plate and allow it to cool.
 9. Add 40 mL of water and 10 mL of concentrated hydrochloric acid to the beaker and cover with a Teflon watch glass.
 - If the sample contains platinum, also add 3 drops of hydrogen peroxide to the beaker to redissolve the platinum.
 10. Return the beaker to the hot plate and bring to a boil.
 11. Remove the beaker from the hot plate and allow it to cool.
 12. Transfer the contents of the beaker, quantitatively using a funnel, to a 200-mL polypropylene volumetric flask.
 13. Pipet 10 mL of 1000- $\mu\text{g/mL}$ scandium solution into the flask as an internal standard.
 - If a spectrometer other than that listed in *APPARATUS* is used, yttrium can be substituted as the internal standard (see Note 1).
 14. Allow the flask to cool to ambient temperature. Then dilute to volume with water. Cap and invert the flask several times to mix thoroughly.
 15. Prepare the matched standard solutions and a calibration blank as described in *Preparation of Calibration Standards*.
 - The preparation of Standard 2 and the analysis of the samples must be completed the same day as the samples are diluted to final volume. The solutions are not stable overnight (silica will precipitate). Standard 1 and the calibration blank are stable for 3 months.

Sample Analysis

Set up the ICP-AES instrument in accordance with the instrument manufacturer's guidelines, allowing the system to equilibrate for at least 30 minutes after the plasma is ignited prior to starting the analysis. Table 1 lists recommended wavelengths for each element. Other wavelengths may be used if it can be shown that precision is not adversely affected (see *PRECISION*). If the recommended spectrometer is used, Myers-Tracy signal compensation must be used. Use of a corrosion resistant sample introduction system is recommended.

1. Standardize the instrument by aspirating the blank, followed by Standards 1 and 2. Allow sufficient wash-out time between aspirations.
 - Wash-out times are dependent on instrument conditions such as pump rate, and on concentration levels being measured, and can vary between 30 and 120 seconds.
2. Aspirate the samples, after first entering the dilution factors into the computer. Allow sufficient wash-out time between aspirations.
3. Aspirate the standards, treating them as samples with no dilution factors, as calibration checks as often as recommended by the instrument manufacturer, but at the very least following aspiration of the final sample.
 - Any calibration checks and the final standard readings should return the concentrations of the elements in the standards within $\pm 5\%$ relative. If not, recalibrate and reaspirate the samples.

CALCULATIONS

If the dilution factor for the sample is entered into the instrument computer, the concentrations of the elements in the original sample in mass-ppm, on an as-received (AR) basis, are calculated by the computer. Divide the mass-ppm values by 10,000 to convert to mass-%. Below 0.10 mass-%, report to two significant figures; at and above 0.10 mass-%, report to three significant figures.

NOTES

1. The choice of an internal standard is dictated by the instrument requirements and the composition of the samples to be analyzed. Some instruments require a specific element (i.e., scandium). Other elements that are commonly used include yttrium, bismuth and rhodium. One requirement is that the internal standard element not be present in the sample at levels above a few mass-ppm. A full discussion of internal standardization is not possible here. For this method, the use of Sc or Y is recommended.

The concentration of the internal standard to be used is dependent on instrument response, wavelength and the concentrations of other elements being ratioed to the internal standard. Use the instrument manufacturer's recommendations, or a compromise concentration of 50 mass-ppm of either Sc or Y, which is mid-range in concentration, versus the other elements being determined by this method.

When using internal standards, a sequential ICP-AES instrument measures element emission intensities in step-wise fashion, moving from one element wavelength to the next. If the internal standard is also read in this way, there will be a time interval between the reading of the internal standard intensity and the subsequent element intensities. During this interval, instrument drift can occur that will lead to error in the analysis. To avoid this, the method specifies use of a sequential instrument that reads the internal standard emission intensity at the same time each element intensity is read; this compensates for any drift in the instrument.

In the case of a simultaneous instrument, the internal standard is read concurrently with all elements of interest, therefore, drift is not a factor. An additional benefit of an internal standard in either case is to compensate for slight differences in matrix conditions between the samples and standards that can arise from small variations in levels of matrix components such as the aluminum and acids (these generally cause slight viscosity and/or nebulization differences).

2. The maximum solubility for silicon in the acid matrix used in this method is 60 mass-ppm in solution, or 1.2 mass-% on the catalyst (alumina supports only). The upper concentration for silicon determination by this method has been placed at 10 mass-ppm in solution, or 0.2 mass-% in the catalyst. If silicon determination above this level is required, use UOP Method 926, which uses a lithium metaborate fusion to solubilize the silicon.

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated at the concentrations shown in Table 2. Two tests performed in one laboratory by different analysts, on different days, should not differ by more than the allowable differences shown (95% probability).

Table 2

Element	Concentration, mass-%, VF	Within-Lab esd, mass-%	Allowable Difference, mass-%
Iron	0.023	0.0009	0.0029
	0.016	0.0005	0.0018
Nickel	0.0084	0.0006	0.0022
Molybdenum	0.019	0.0009	0.0036
Tungsten	0.021	0.0020	0.0066
Cerium	0.0048	0.0006	0.0021
Calcium	0.024	0.0007	0.0025
	0.0031	0.0003	0.0011
Magnesium	0.011	0.0003	0.0010
	0.0016	0.0001	0.0004
Sodium	0.0030	0.0004	0.0015
Vanadium	0.0042	0.0002	0.0005
Cobalt	0.0062	0.0003	0.0013
Titanium	0.0024	0.0002	0.0006
Silicon	0.019	0.0009	0.0030

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is 4 hours. The labor requirement is 1.5 hours.

REFERENCE

UOP Method 926, "Aluminum and Silicon in Fresh Catalysts by Lithium Metaborate Fusion/ICP-AES"

SUGGESTED SUPPLIERS

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)

Inorganic Ventures, Inc., 195 Lehigh Ave., Suite 4, Lakewood, NJ 08701 (908-901-1900)

Johnson Matthey Catalog Co., Inc., Alfa Products, P.O. Box 8247, Ward Hill, MA 01835-0747 (508-521-6300)

Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)

Omega Engineering, Inc., One Omega Dr., P.O. Box 4047, Stamford, CT 06907 (203-359-1660)

Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859-0270 (203-834-6281)

SPEX Industries, Inc., 3880 Park Ave., Edison, NJ 08820 (201-549-7144)