

ALUMINUM AND SILICON IN FRESH CATALYSTS BY LITHIUM METABORATE FUSION/ICP-AES

UOP Method 926-92

SCOPE

This method is for determining aluminum and/or silicon in fresh silica-alumina supported catalysts of known composition by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The method is suitable for aluminum determination over a range of 1 to 53 mass-%, and silicon determination over a range of 1 to 47 mass-%.

OUTLINE OF METHOD

Samples are ground using UOP Method 918 and fused with lithium metaborate. The fusion melt is dissolved in dilute hydrochloric acid. The resulting sample solution is aspirated into an ICP-AES instrument and the concentrations of aluminum and silicon are determined by comparison to matrix-matched standard solutions. Sample results are reported on a volatile-free basis using either UOP Method 275 or UOP Method 412 (base metal catalysts only). Results may also be reported on an oxide 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

Balance, top-loading, readability 0.01-g

Beaker, Vycor, 250-mL

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

Bottles, 125- and 250-mL, narrow mouth, round, polypropylene, Fisher Scientific, Cat. Nos. 02-893-5C and 02-893-5D, respectively

Bottle, washing, one-liter, polypropylene, Fisher Scientific, Cat. No. 03-409-14C

Burner, blast, Meker, Universal, Fisher Scientific, Cat. No. 03-910-5

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.

Crucible, high form, platinum, 30-mL, Fisher Scientific, Cat. No. 08-030E

Cylinders, graduated, 50- and 100-mL

Desiccating cabinet, dry box, Fisher Scientific, Cat. No. 08-647-26

Flasks, volumetric, Class A, 100-, 200-, 250- and 1000-mL, several of each required

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

Gloves, polyethylene

Hot plate, stirring, 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.

Muffle furnace, capable of 1000°C. The interior surface of the furnace must be of non-flaking material, or sample contamination will result.

Oven, drying, capable of 105°C, Fisher Scientific, Cat. No. 13-261-40

Pipets, total volume, Class A, 5-, 10-, 15-, 20- and 25-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

Stirbar, magnetic, Teflon coated, disposable, 3 x 12 mm, Fisher Scientific, Cat. No. 14-511-60A

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

Tongs, crucible, stainless steel, lock joint, platinum shoes, Fisher Scientific, Cat. No. 15-205

Triangle, iron wire, clay covered, Fisher Scientific, Cat. No. 15-285B

Tripod, iron, threaded legs, plain, Fisher Scientific, Cat. No. 15-300B

Watch glass, borosilicate glass, 90-mm diameter

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 deionized or distilled water.

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

Aluminum solution, 10,000-µg/mL, Inorganic Ventures, Cat. No. CGAL10-5

Aluminum solution, 1000-µg/mL, Inorganic Ventures, Cat. No. CGAL1-5

Argon, 99.995% minimum purity, ICP feed gas

Hydrochloric acid, concentrated

Hydrochloric acid, 5% (vol/vol). Mix one part concentrated hydrochloric acid with nineteen parts water. Make one liter at a time and store in a one-liter wash bottle.

Lithium metaborate, SPEX Industries, Cat. No. LI70-454. In areas of high humidity, this material should be dried at 105°C before each use and kept in a dry box.

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

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

Scandium solution, 500-µg/mL. Pipet 50 mL of 1000-µg/mL scandium solution into a 100-mL volumetric flask and dilute to volume with 5% hydrochloric acid. Cap and invert several times to thoroughly mix.

Silica powder, 99.9995% purity, SPEX Industries, Cat. No. SI80-20. In areas of high humidity, this material should be dried at 105°C before each use and kept in a dry box.

Yttrium solution, 1000-µg/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 Calibration Standards

Aluminum Standard, 250-µg/mL

1. Weigh, to the nearest 0.01 g, 1.0 g of lithium metaborate into a 200-mL volumetric flask, using a top-loading balance.
2. Pipet 50 mL of 1000-µg/mL aluminum solution into the flask.
3. Add approximately 100 mL of 5% hydrochloric acid to the flask.
4. Add 10 mL of 1000-µg/mL scandium solution to the flask as an internal standard (see Note 1).
 - If a spectrometer other than that listed in *APPARATUS* is used, yttrium can be substituted as the internal standard (see Note 1).
5. Heat the flask gently in a warm water bath (40 to 50°C), if required, to dissolve the lithium metaborate.
6. Allow the flask to cool to ambient temperature and dilute to the mark with 5% hydrochloric acid. Cap and invert several times to mix thoroughly, and then transfer the solution to a 250-mL polypropylene bottle.

Silicon Standard, 200-µg/mL

1. Weigh, to the nearest 0.1 mg, 0.1070 g of silica powder, previously dried at 105°C, into an undamaged platinum crucible.
 - Crucibles having creases or folds can entrap materials, causing incomplete dissolution of the fusion melt and/or carryover to the next sample.

2. Using a top loading balance, add 1.25 g, weighed to the nearest 0.01 g, of lithium metaborate to the crucible. Rotate and tilt the crucible to thoroughly mix the contents.
3. Place the crucible in a 1000°C muffle furnace for 30 minutes, or on a tripod and melt the mixture using a blast type burner. Carefully check to see that the melt is clear, with no silica particles remaining unfused.
 - An incomplete melt will result in a standard of less than 200-µg/mL and cause sample results to be high.
4. Remove the crucible from the flame or furnace with platinum tipped tongs, place it upright in a 250-mL Vycor beaker and allow to cool for five minutes.
5. Place a stirbar inside the crucible and add a sufficient amount of 5% hydrochloric acid to cover the crucible by about 10 mm.
6. Cover the beaker with a watch glass and place it on a stirring hot plate at 150°C (as measured with a surface probe). Bring the solution to a boil while stirring, and boil until the fusion melt has completely dissolved, usually about 10 minutes after boiling begins. Check the crucible carefully to ensure that all the melt has dissolved.
 - If any silica remains undissolved, start over with Step 1.
7. Remove the beaker from the hot plate and allow it to cool. Then quantitatively transfer the contents to a 250-mL volumetric flask using 5% hydrochloric acid from a wash bottle and a funnel.
 - The crucible remains in the beaker. Use the wash bottle to wash the interior and exterior walls of the crucible as well as the beaker walls during transfer.
8. Pipet 25 mL of 500-µg/mL scandium solution into the flask as an internal standard (see Note 1).
 - If a spectrometer other than that listed in *APPARATUS* is used, yttrium can be substituted as the internal standard (see Note 1).
9. Allow the solution to cool to ambient temperature and then dilute to the mark with 5% hydrochloric acid. Cap and invert several times to mix thoroughly and then transfer the solution to a 250-mL polypropylene bottle.

Calibration Blank

Prepare a calibration blank at the same acid and lithium metaborate levels, with the internal standard added, but without any aluminum or silicon.

- The standards and blank are stable for three months.
- A blank is necessary due to trace levels of silicon, and occasionally aluminum, found in commercial batches of lithium metaborate.

Sample Preparation

1. Grind the sample to less than 80 mesh using UOP Method 918.
2. Weigh, to the nearest 0.01 g, 1.0 g of lithium metaborate into a platinum crucible, using a top-loading balance.
3. Shake the sample bottle randomly by hand for 5 minutes to avoid errors caused by stratification due to settling of the ground sample in the bottle, then proceed immediately with Step 4.
4. Weigh, to the nearest 0.1 mg, 0.1 to 0.2 g of ground sample into the platinum crucible on top of the lithium metaborate. Rotate and tilt the crucible by hand to mix the sample with the lithium metaborate.

- If the results are to be reported on a volatile-free basis, weigh a sample portion for LOI by either UOP Method 275 or UOP Method 412 (base metal catalysts only) at the same time the sample is weighed for the metal determination. Samples containing reduced metals may yield mass gains rather than losses.
 - Sample size varies between 0.1 and 0.2 g, depending on the catalyst's composition. At near equal proportions of silica and aluminum, use 0.2 g. As the concentrations of the two elements diverge, use less sample to a minimum of 0.1 g at silicon or aluminum concentrations below 10 mass-%.
5. Place the crucible in a 1000°C muffle furnace or over the flame of a blast type burner (see Note 2). Heat for about 30 minutes, checking occasionally for unfused sample.
 - If unfused sample is detected, rotate and tilt the hot crucible using the tongs, and return to the muffle or burner until fusion is complete.
 6. Remove the crucible from the flame or furnace with platinum-tipped tongs, place it upright in a 250-mL Vycor beaker and allow to cool for five minutes.
 7. Add, with a graduated cylinder, sufficient 5% hydrochloric acid to the beaker to cover the crucible by about 10 mm.
 8. Place a stir bar in the crucible, cover the beaker with a watch glass, and place the beaker on a stirring hot plate, adjusting the heat to achieve mild boiling and the stirrer to achieve a vortex in the solution.
 9. Continue heating until the fusion melt is completely dissolved, usually within 10 minutes after boiling begins.
 - Check the crucible carefully for any remaining residue of the fusion melt or unfused sample. If any doubt remains as to the completeness of the fusion or dissolution of the melt, discard the solution and start the test over with Step 2.
 - Catalysts containing tungsten will yield a solution with a yellow precipitate. This precipitate can be ignored.
 10. Remove the beaker from the hot plate and allow it to cool. Then quantitatively transfer the contents of the beaker to a 200-mL volumetric flask using a funnel and 5% hydrochloric acid from a wash bottle.
 - The crucible remains in the beaker. Use the wash bottle to wash the interior and exterior walls of the crucible as well as the beaker walls during transfer.
 11. Pipet 10 mL of 1000-µg/mL scandium solution into the flask as an internal standard (see Note 1).
 - If a spectrometer other than that listed in *APPARATUS* is used, yttrium can be substituted as the internal standard (see Note 1).
 12. Allow the solution to cool to ambient temperature and dilute to the mark with 5% hydrochloric acid. Cap and invert several times to thoroughly mix.

Sample Analysis

Set up the ICP-AES instrument in accordance with the instrument manufacturer's guidelines, allowing at least 30 minutes for equilibration after plasma ignition 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.

1. Standardize the instrument by aspirating the blank, followed by the standards. Allow sufficient wash-out time between aspirations.
 - Wash-out times depend on instrument conditions such as pump rate, and on the 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.
 - Solutions resulting from dissolution of tungsten containing catalysts will contain a yellow precipitate. Allow the precipitate to settle, and do not allow the ICP sampling tube to contact the precipitate, because the tubing or nebulizer may clog.
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 reading should return the concentrations of the Al or Si in the standards within $\pm 3\%$ relative. If not, recalibrate and reaspirate the samples.

Table 1
Recommended Wavelengths

<u>Element</u>	<u>Wavelength, nm</u>
Al	396.152
Si	251.611
Sc	424.683

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-%, on an as-received (AR) basis are calculated by the computer. Report the results to three significant figures at one mass-% and above, to two significant figures below one mass-%.

If the LOI is available prior to the instrumental analysis, the sample mass can be adjusted for it, and the adjusted dilution factor entered into the instrument computer. The computer will then print out the concentrations on a volatile-free basis. If not, calculate the concentration of aluminum and silicon in the original sample on a volatile-free (VF) basis as follows:

$$\text{Element, mass-\%, VF} = \frac{100K}{100_A - L}$$

where:

K = concentration of element in original sample, mass-% AR, from instrument printout

L = LOI at 900°C or 500°C as determined by UOP Method 275 or 412, mass-%

100 = factor to calculate mass-%

100_A = factor to convert to mass-% residue after ignition

If required, use the gravimetric factors listed in Table 2 to convert the element concentrations to oxide equivalents.

Table 2
Gravimetric Factors

<u>To Convert</u>	<u>Multiply By</u>
Si to SiO₂	2.13936
Al to Al₂O₃	1.88946

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. The 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 inadvertent small variations in levels of matrix components such as the aluminum and acids (these generally cause slight viscosity and/or nebulization differences).

2. Use of an automated fusion device is permitted. Most devices require the addition of wetting agents (i.e., potassium iodide) to the crucibles to ensure complete transfer of the hot fusion melt from the crucible to the dissolution beakers. Any wetting agents added to the samples must also be added to the standards to maintain a matrix match. The crucible contents should be carefully examined to ensure that the total sample has been properly fused and that the fusion melt has been quantitatively transferred to the dissolution beaker. The *PROCEDURE* section needs to be modified for use with such a device.

PRECISION

Repeatability

Based on two tests 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 3. 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 3

Element	Concentration, mass-%, VF	Within-Lab esd, mass-%	Allowable Difference, mass-%
Silicon	21.3	0.08	0.3
Aluminum	28.2	0.08	0.3

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.

REFERENCES

UOP Method 275, "Loss on Ignition of Catalysts at 900°C"

UOP Method 412, "Loss on Ignition of Catalysts at 500°C"

UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis"

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)

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)