



Nickel, Molybdenum, Phosphorous, Cobalt, and Aluminum in Fresh Catalysts by ICP-OES

UOP Method 925-16

Scope

This method is for determining nickel, molybdenum, phosphorus and cobalt in fresh *gamma*-alumina supported catalysts; and nickel (Ni), molybdenum (Mo), phosphorus (P), cobalt (Co) and aluminum (Al) in fresh silica-alumina supported catalysts of known composition by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The method is suitable for determining nickel over a range of 1 to 10 mass-%, molybdenum over a range of 5 to 20 mass-%, phosphorus (as phosphate only) over a range of 0.5 to 25 mass-%, cobalt over a range of 1 to 5 mass-%, and aluminum over a range of 5 to 50 mass-%. Catalysts containing *alpha*- or *theta*-alumina phases cannot be analyzed by the method. Nickel bearing catalysts that contain tungsten are analyzed by UOP Method 924.

References

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

UOP Method 924, "Nickel, Tungsten and Aluminium in Fresh Catalysts by ICP-AES,"
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

Perkin Elmer WinLab32 for ICP Instrument Control Software Manual

Outline of Method

Samples are ground using UOP Method 918, with alumina supported samples being dissolved using sulfuric acid, while silica-alumina supported samples are dissolved using sulfuric and hydrofluoric acids. The resulting sample solution is aspirated into an ICP-OES instrument and the element concentrations determined by comparison to a matrix-matched standard solution. Sample results are reported on a volatile-free basis, based on a 500 °C LOI (UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents"). Aluminum is determined on silica-alumina supported catalysts only. If desired, the results can be reported on an oxide basis also.

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) 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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Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP 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.

Apparatus

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

Balance, readable to 0.0001 g

Beaker, quartz, low form, 250-mL, Ace Glass, Inc., Cat. No. 5334-14

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

Crucible, wide form, 17 mL, porcelain, Coors No. 60135, Fisher Scientific, Cat. No. FB-965-J

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

Flasks, volumetric, Class A, 100-, 200-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 13-756-694, -695, -697 and -698, respectively, several of each required

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

Hot plate, variable heat to at least 400 °C, Fisher Scientific, Cat. No. 11-100-49H

Inductively Coupled Plasma-Optical Emission Spectrometer, computer controlled, having a bandpass of 0.010 nm (FWHM) or better, and covering the wavelength range specified in Table 2. 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 7300DV spectrometer with a corrosion resistant sample introduction system, or its equivalent, is required.

Pipets, total volume, Class A, 5-, 7-, 8-, 10-, 15-, 20-, 25-, 30- and 50-mL, Fisher Scientific, Cat. Nos. 13-660-5E, 13-646-42, -43, 13-660-5F, -5M, -5H, -5J, -5S, and -5K, several of each required. Alternatively, a digital pipettor may be used.

Pipets, total volume, 1-5 mL, 1-10mL, Eppendorf pipet Cat. No. 4920000105, 4920000113

Pipet filler, Fisher Scientific, Cat. No. 13-681-102A

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

Watch glass, 100-mm, glass, for 250-mL beaker, Fisher Scientific, Cat. No. 02-612D

Watch glass, 100-mm, PTFE, Cat. No. 02-617-1E

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 deionized or distilled water.

Aluminum solution, 1000-μg/mL, Spex Certiprep, Inc, Cat. No. PLAL2-2X

Argon, 99.995% minimum purity, ICP feed gas

Cobalt solution, 1000-μg/mL, Spex Certiprep, Inc, Cat. No. PLCO2-2X

Gloves, neoprene, Fisher Scientific, Cat. Nos. 11-391-129A through -129E for sizes 7 through 10, respectively

Hydrofluoric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0628-7

Molybdenum solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Inc, Cat. No. PLMO9-2X

Nickel solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Inc, Cat. No. PLNI2-2X

Nitric acid, concentrated, trace metals grade, VWR, Cat. No. EM-NX0408-2

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

Phosphorus solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Inc, Cat. No. PLP9-2X

Scandium metal solution, aqueous, 10,000- $\mu\text{g/mL}$, SPEX CertiPrep, Inc., Cat. No. PLSC2-3X, for use as an internal standard

Scandium internal standard, aqueous, 100- $\mu\text{g/mL}$. To prepare 100 mL, pipet 1 mL of the 10,000- $\mu\text{g/mL}$ 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.

Sulfuric acid, concentrated, trace metals grade, VWR, Cat. No. EM-SX1248-6

Yttrium solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Inc, Cat. No. PLY2-2X. Not required if the spectrometer specified in *Apparatus* is used.

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. Consult 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. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations.

Preparation of Calibration Standards

Since the catalyst composition is known, a single standard may be prepared and used that matches the composition of the catalyst. The concentrations of nickel, molybdenum, phosphorus, cobalt and/or aluminum are determined by calculation. For adequate calibration the sample must be within $\pm 10\%$ (relative) of the standard concentration. Each catalyst type must have its own standard, matched to the catalyst composition. For example, for a catalyst with a nominal composition of 4 mass-% nickel oxide, 24 mass-% molybdenum trioxide, 65 mass-% alumina and 7 mass-% phosphorous pentoxide, and using an original sample mass of 0.2 g diluted to 500 mL; the resulting sample solution would contain approximately 12- $\mu\text{g/mL}$ nickel, 65- $\mu\text{g/mL}$ molybdenum, 140- $\mu\text{g/mL}$ aluminum and 15 $\mu\text{g/mL}$ phosphorous. A standard would be prepared as close as possible to those nickel, molybdenum aluminum and phosphorous concentration. See Table 1 for recommended dilutions to be used for different nickel, molybdenum and phosphorous concentrations on the catalyst. Prepare a standard for the above example as follows:

1. Pipet 2 mL of 1000- $\mu\text{g/mL}$ nickel solution, 7.5 mL of 1000- $\mu\text{g/mL}$ molybdenum solution, 15 mL of 1000- $\mu\text{g/mL}$ aluminum solution and 2 mL of 1000- $\mu\text{g/mL}$ phosphorous solution into a 100-mL volumetric flask.
2. Add 2 mL of sulfuric acid.
3. Pipet 2 mL of 100- $\mu\text{g/mL}$ scandium solution into the flask as an internal standard (see *Notes*).

- If a spectrometer other than that listed in *Apparatus* is used, yttrium can be substituted as the internal standard.
4. Allow the flask to cool to ambient temperature and dilute to volume with water. Cap and invert several times to mix thoroughly.
 - A standard prepared in this fashion will contain 20- $\mu\text{g/mL}$ nickel, 75- $\mu\text{g/mL}$ molybdenum and 150- $\mu\text{g/mL}$ aluminum, 20- $\mu\text{g/mL}$ phosphorous and is stable for one month.
 5. Prepare a calibration blank at the same acid levels and with the internal standard added, but without any nickel, molybdenum, aluminum or phosphorous. Hydrofluoric acid is not required for blank.
 - 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
Recommended Sample Dilution

<u>Concentration, mass-%</u>					<u>Sample mass per 200 mL</u>
<u>Al</u>	<u>Ni</u>	<u>Mo</u>	<u>P</u>	<u>Co</u>	
16-24	1 - 10	5 - 20	2 - 7	1 - 5	0.4 g
35-45	na	na	7 - 25	na	0.2 g

na= not applicable for this element

Sample Preparation

1. Grind the sample to less than 80 mesh using UOP Method 918.
2. Mix the contents well, by hand for at least 30 seconds to avoid errors caused by stratification due to settling of the ground sample in the bottle, then proceed immediately with Step 3.
3. Weigh, to the nearest 0.0001 g, the appropriate mass of ground catalyst into a 250-mL PTFE beaker (see Table 1).
 - If the results are to be reported on a volatile-free basis, weigh a sample portion for LOI by UOP Method 954 at the same time the sample is weighed for the metal determination.
 - If the catalyst support is alumina only, a quartz beaker may be used.
4. Using a graduated cylinder, add 25 mL of water to the beaker to wet the catalyst.
5. Using a graduated cylinder, slowly add 10 mL of sulfuric acid to the beaker, and swirl to mix the contents.
 - Add the acid slowly to avoid spattering.
6. If the catalyst support is silica-alumina, add 5 mL of concentrated hydrofluoric acid to the beaker, using a graduated polypropylene cylinder. Otherwise skip this step.
 - Appropriate safety precautions must be taken when handling hydrofluoric acid.
7. Place the beaker on a hot plate and adjust the heat to achieve mild boiling. For alumina supports only, heat until the sample is completely dissolved, then proceed to Step 9.
8. Continue heating while slowly increasing the temperature until the evolution of thick white fumes, characteristic of sulfuric acid.
 - Heating to sulfuric acid fumes eliminates all silicon as the tetrafluoride and any residual HF from the solution. DO NOT EXCESSIVELY FUME THE SAMPLES! Doing so will make it difficult to matrix match the standards with respect to acid level.

- When using PTFE beakers, do not exceed a hot plate temperature of 250°C, as measured with a surface probe, or the beaker will deform and/or melt.
9. Remove the beaker from the hot plate, cool, and then carefully add approximately 40 mL of water to the beaker. Cover the beaker and return it to the hot plate.
 10. Heat to a mild boil, and then remove the beaker from the hot plate and allow it to cool.
 11. Using a funnel, transfer the contents of the beaker, quantitatively with water, into a 500-mL volumetric flask containing approximately 100 mL of water.
 12. Allow the flask to cool to ambient temperature.
 13. Pipet 10 mL of 100-µg/mL scandium solution into the flask as an internal standard
 14. Dilute to volume with water, and cap and invert the flask several times to mix thoroughly.
 15. Using the sample dilution range, and the known composition of the catalyst, prepare the matched standard solution and a calibration blank in a manner similar to the example shown in *Preparation of Calibration Standards*.

Sample Analysis

Set up the ICP-OES 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- 2 lists recommended wavelengths for the elemental determinations. Other wavelengths may be used if it can be shown that method precision is not adversely affected (see *Precision*). Use of a corrosion resistant sample introduction system is recommended.

1. Standardize the instrument by aspirating the blank followed by the standard. Allow sufficient wash-out time between aspirations.
2. Aspirate the samples, after first entering the dilution factors into the computer. Allow sufficient wash-out time between aspirations.
3. Aspirate the standard, treating it as a sample with no dilution factor, as a calibration check. This should be done as often as recommended by the instrument manufacturer, but minimally after every 4-5 samples and after the final sample.
 - Any calibration checks and the final standard reading should return the concentrations of the Ni, Mo, P, Co and/or Al in the standard within $\pm 3\%$ relative. If not, recalibrate and reaspirate the samples.

Table 2
Recommended Wavelengths

<u>Element</u>	<u>Wavelength, nm</u>
Ni	231.604
Mo	204.597
P	214.913
Co	238.892
Al	396.152
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, on an as-received (AR) basis are calculated by the computer. Report the results to three significant figures.

If the LOI determination is completed prior to the instrumental analysis, the sample mass can be corrected to volatile-free, and that value entered into the instrument computer yields the elemental concentrations on a volatile-free basis. If the LOI determination is completed after the instrumental analysis, calculate the concentration of nickel, molybdenum, phosphorus, cobalt and/or aluminum in the original sample on a volatile-free (VF) basis using Equation 1:

$$\text{Element, mass-\%} = \frac{100K}{100_A - L} \quad (1)$$

where:

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

L = LOI at 500°C as determined by UOP Method 954, mass-%

100 = factor to calculate mass-%

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

If desired, the elemental results can be reported as oxides. Multiply by the appropriate gravimetric factors listed in Table 3.

Table 3
Gravimetric Factors

<u>To Convert</u>	<u>Multiply By</u>
Ni to NiO	1.27254
Mo to MoO ₃	1.50031
P to P ₂ O ₅	2.29136
Co to Co ₃ O ₄	1.36197
Al to Al ₂ O ₃	1.88946

Notes

The choice of an internal standard is scandium or yttrium, dictated by the composition of the samples to be analyzed. The requirement is that the internal standard element not be present in the sample. A discussion of internal standardization can be found in the Perkin Elmer WinLab32 for ICP Instrument Control Software manual, Chapter 12, Calibration and Calculations.

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 2 mass-ppm of either Sc, or Y, which is mid-range in concentration versus the other elements being determined by this method.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an auto sampler.

Repeatability and Site Precision

A nested design was carried out for determining metals in two catalyst samples by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 16 analyses. An example of variability for a select catalyst samples using a stepwise analysis of variance procedure, the within-day and within-lab 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 site precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and Site Precision, mass-%

	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Aluminium	33.89	0.163	0.640	0.197	0.889
Molybdenum	16.30	0.132	0.519	0.158	0.621
Nickel	3.26	0.035	0.139	0.050	0.196
Phosphorous	3.18	0.035	0.139	0.035	0.139

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 is 1.5 hours.

Suggested Suppliers

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

Omega Engineering, Inc., One Omega Dr., P.O. Box 4047, Stamford, CT 06907, USA, 1-203-359-1660, www.omega.com

PerkinElmer Analytical Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794, USA, 1-203-925-4600, www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA, 1-732-549-7144,
www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com