

NOBLE METALS AND MODIFIERS IN CATALYSTS BY ICP—AES

UOP Method 873-86

SCOPE

This method is for determining platinum, rhodium and rhenium, in fresh and regenerated catalysts composed of alumina or silica/alumina by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Additionally, modifiers such as tin, indium, lithium, potassium, cerium and lanthanum can also be determined. Platinum and rhenium can be determined within the concentration range of 0.1 to 1.0 mass-% when a 1-g sample of catalyst is used for the analysis, while rhodium can be determined down to 0.01 mass-%. The tin, indium and lithium concentration range is generally 0.1 to 0.7 mass-%. Potassium, cerium and lanthanum can be determined from 0.5 to several mass-%. The method is sufficiently flexible to add more elemental analyses if needed.

OUTLINE OF METHOD

The samples are dissolved in acid and then scandium is added to the solution as internal standard. The sample solutions are then aspirated into a computer controlled ICP-AES along with appropriate, matrix-matched standards. Concentrations are determined by comparison of the sample emission ratios to the computer-generated standard calibration curves.

APPARATUS

Balance, readability 0.1-mg

Beaker, Teflon, 250-mL

Beaker, borosilicate glass, 250-mL

Catalyst Grinding Equipment

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

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

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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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.

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

Flask, volumetric, 1000-, 200- and 100-mL capacity

Hot plate, variable heat to 400 C

Muffle furnace, capable of operation at 1000 C

Pipets, volumetric, transfer, Class A, 50-, 25-, 20-, 10-, 5-, 2- and 1-mL

Regulator, argon, two-stage, high purity, Matheson, Model 3104-580, or equivalent

Regulator, nitrogen, two-stage, high purity, Matheson, Model 3104-580, or equivalent

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

Watch glass, borosilicate glass, 100-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 ASTM D 1193 Type I reagent grade water.

Aluminum oxide, powder, available from SPEX Industries, Inc., Cat. No. AL57, or equivalent

Argon, 99.995% minimum purity

Hydrochloric acid, concentrated

Hydrofluoric acid, concentrated

Hydrogen peroxide, 30%

Nitrogen, 99.99% minimum purity

Phosphoric acid, concentrated, 85%

Sulfuric acid, concentrated

Scandium solution, aqueous, 1000 mass-ppm, SPEX Industries, Inc., Cat. No. PLSC-2, or equivalent

Standard metal solutions, Pt, Rh, Re, Sn, In, Li and K solutions of 1000 mass-ppm concentrations, and Ce and La solutions of 10,000 mass-ppm concentrations, SPEX Industries, Inc., Cat. Nos. PLPT-2, PLRH-2, PLRE-2, PLSN-2, PLIN-2, PLLI-2, PLK-2, PLCE-3X and PLLA-3X, respectively, or equivalent

PREPARATION AND STANDARDIZATION OF APPARATUS

Preparation of Standards

Prepare standards at approximately the concentrations shown in Table 2 by appropriate dilution of the standard metal solutions. Due to the linear response of the ICP, single point standards can be used. Prepare the standards in the same matrix as the samples, see *Sample Preparation*. Also prepare a blank having the same matrix. Separate standards and blanks are required for each sample dissolution matrix.

Table 1 Elements Sought		Table 2 Recommended Standard Concentrations, mass-ppm			
Element	λ , nm	Element	gamma alumina	automotive	alpha alumina
Pt	265.945	Pt	40.0	15.0	20.0
Rh	343.489	Rh	5.0	5.0	
Re	197.313	Re	25.0		
Sn	189.989	Sn	25.0		20.0
In	230.606	In	20.0		
Li	670.781	Li	30.0		15.0
K	766.490	K	150.0		
Ce	393.109	Ce		600.0	
La	379.478	La		300.0	
Sc	424.683	Sc	50.0	50.0	50.0

Preparation of the Spectrometer

Start up the ICP-AES and ignite the plasma according to the manufacturer's recommendations. Allow a minimum of 30 minutes warm up after the plasma is ignited before starting the analysis. Perform a wavelength calibration prior to the start of the analysis, if recommended by the manufacturer. Aspirate the standards and blank to establish the calibration curves prior to aspiration of the samples. Table 1 lists recommended wavelengths to be used for the analyses.

PROCEDURE

Sample Preparation

gamma-Alumina Catalyst

Weigh approximately $1.0 \text{ g} \pm 0.1 \text{ mg}$ of sample (whole pills) into a tared 250-mL beaker; add 10 mL of water, 10 mL of concentrated sulfuric acid, one drop of concentrated hydrochloric acid and two drops of 30% hydrogen peroxide. Cover the beaker with a watch glass, place it on the hot plate in a hood or well-ventilated area and bring it to a mild boil. Dissolution takes about 15 minutes. Remove the covered beaker from the hot plate and allow it to cool. Add 20 mL of water, 40 mL of concentrated hydrochloric acid, two drops of 30% hydrogen peroxide, cover with the watch glass, and return to the hot plate. Boil for an additional 10 minutes to remove any residual peroxide. Allow the beaker to cool and transfer the contents quantitatively to a 200-mL volumetric flask. Rinse the beaker and watch glass several times with water and

transfer the washings to the volumetric flask. Add 10 mL of 1000 mass-ppm scandium solution to the flask and bring to volume with water.

Automotive Catalyst

Grind the sample for 5 minutes on the mixing mill, using the tungsten carbide containers and two grinding balls. Weigh approximately $1.0 \text{ g} \pm 0.1 \text{ mg}$ of ground sample into a tared 250-mL Teflon beaker. Add 5 mL of water, 10 mL of concentrated sulfuric acid and 10 mL of concentrated hydrofluoric acid. Place on the hot plate in a hood or well-ventilated area and bring to a mild boil without a cover. Continue the heating until the evolution of white sulfur trioxide fumes indicates that all HF has evolved. Remove the beaker from the hot plate and allow it to cool. Add 20 mL of water, 20 mL of concentrated hydrochloric acid, two drops of 30% hydrogen peroxide, cover with a watch glass, and return to the hot plate. Boil for an additional 10 minutes to remove any residual peroxide. Allow the beaker to cool and transfer the contents quantitatively to a 100-mL volumetric flask, rinsing the beaker and watch glass several times with water. Add 5 mL of 1000 mass-ppm scandium solution to the flask and bring to volume with water.

alpha-Alumina Catalyst

Grind the sample for 5 minutes on the mixing mill, using the tungsten carbide containers and two grinding balls. Weigh approximately $0.6 \text{ g} \pm 0.1 \text{ mg}$ of ground sample into a tared 250-mL borosilicate glass beaker. Add 10 mL of concentrated sulfuric acid and 10 mL of concentrated phosphoric acid. Cover with a watch glass, place on the hot plate in a hood or well-ventilated area and bring to a mild boil. Continue the heating until the sample is completely dissolved. Swirl occasionally to make sure that no undissolved sample powder has clung to the sides of the beaker. Remove the beaker from the hot plate and allow it to cool to ambient temperature. Add 10 mL of water, 10 mL of concentrated hydrochloric acid and 3 to 4 drops of 30% hydrogen peroxide. Cover with the watch glass, swirl to mix the contents, and return to the hot plate. Boil for an additional 10 minutes to remove any residual peroxide. Allow the beaker to cool and quantitatively transfer the contents to a 100-mL volumetric flask, rinsing the beaker and watch glass several times with water. Add 5 mL of 1000 mass-ppm scandium solution to the flask and bring to volume with water.

Spectrometric Procedure

Follow the procedures described under *Preparation of Spectrometer*. Following aspiration of the standards and blank, aspirate the samples after entering the appropriate mass per volume in the computer. The computer will calculate the mass-% metal in the original sample, and print the result.

If the results are to be reported on a volatile-free basis, determine a loss on ignition (LOI) on the sample at 900 C. The LOI must be determined on whole pills for gamma-alumina, or the ground sample for automotive and alpha-alumina. The catalyst must be sampled for LOI and metals analysis at the same time to avoid errors resulting from the absorption of moisture.

CALCULATIONS

Calculate the mass-% of each element in the sample, as received, using the following equation:

$$C = \frac{R}{10^4 W}$$

where:

C = concentration of a specific element in original sample, mass-%

R = concentration of element in diluted sample, from instrument readout, mass-ppm

W = mass of sample used/diluted volume (either 100- or 200-mL depending on dissolution scheme), g/mL

10⁴ = conversion factor, mass-ppm to mass-%

If the value is to be reported on a volatile-free basis, replace W in the above equation with W(VF), which is calculated as follows:

$$W(VF) = \frac{W(100 - L)}{100}$$

where:

L = loss on ignition at 900 C, mass%

W = previously defined

W(VF) = mass of sample adjusted for loss on ignition/diluted volume (either 100- or 200-mL depending on dissolution scheme), g/mL

These calculations are normally performed by the computer software utilizing the internal standard, after the analyst enters the appropriate value for W. If the LOI is available before the sample solution is aspirated into the plasma, the value for W(VF) can be entered, and the computer will then print out the concentration of metal in the original sample on a volatile-free basis.

PRECISION

The estimated standard deviations (esd) for various metals and concentration levels are shown in the following table. Duplicate results by the same operator should not differ by more than the amounts shown in the “allowable difference” column (95% probability).

Matrix and Metal	Concentration Level, mass-%	Number of Replicates	esd, mass-%	Allowable Difference, mass-%
<u>gamma-Alumina</u>				
Tin	0.27	6	0.0095	0.035
Tin	0.46	6	0.0085	0.031
Platinum	0.37	6	0.0042	0.015
Platinum	0.73	6	0.0069	0.025
Rhodium	0.048	6	0.0005	0.0019
Indium	0.39	6	0.0037	0.013
Lithium	0.18	6	0.0024	0.0088
Lithium	0.63	6	0.0090	0.033
Potassium	2.52	6	0.025	0.089

Matrix and Metal	Concentration Level, mass-%	Number of Replicates	esd, mass-%	Allowable Difference, mass-%
<u>Automotive</u>				
Lanthanum Oxide	2.52	6	0.032	0.117
Cerium Oxide	7.30	6	0.095	0.344
Platinum	0.12	6	0.0042	0.015
<u>alpha-Alumina</u>				
Tin	0.32	6	0.0016	0.0058
Lithium	0.18	6	0.0030	0.011
Platinum	0.20	6	0.0028	0.010

TIME FOR ANALYSIS

The elapsed time for one analysis is 3 hours. The labor requirement for one analysis is 1.5 hours, or in groups of 5 or more samples, 1.3 hours.

REFERENCE

ASTM Method D 1193, www.astm.org

SUGGESTED SUPPLIERS

Matheson, P.O. Box 96, Joliet, IL 60434
SPEX Industries, Inc., P.O. Box 798, Metuchen, NJ 08840