



A Honeywell Company

Platinum in Fresh Catalysts by Spectrophotometry

UOP Method 274-13

Scope

This method is for determining platinum in fresh gamma-alumina, theta-alumina, or silica/gamma-alumina catalysts at concentrations from approximately 0.05 to 1.0 mass-% by spectrophotometry. Catalysts containing rhenium cannot be analyzed by this method. Any other elements that produce colored ions in the dissolution or color-development steps constitute a positive interference. These include chromium, rhodium, cobalt and molybdenum, but other elements can also interfere.

References

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

All three types of fresh catalyst are sampled and ground as described in UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis." gamma-Alumina catalyst can be digested by either hot plate digestion or by microwave digestion. theta-Alumina catalyst is digested by microwave digestion. Silica/gamma-alumina catalyst must be digested by hot plate. Silica is removed from silica-containing catalysts as silicon tetrafluoride by fuming with hydrofluoric and sulfuric acid in a Teflon beaker on a hot plate, according to a specified procedure. After the sample has been digested by the applicable technique and the platinum dissolved, a hydrochloric acid solution of stannous chloride is added to the platinum solution to produce a yellow color and spectrophotometric measurements are made at 403 nm. The concentration of the platinum is determined by comparing the absorbance of the sample solution to a standard calibration curve prepared from matrix-matched, platinum-stannous standard solutions. The platinum concentration is corrected to a volatile-free basis from an LOI at 700 or 900°C by UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," depending on catalyst composition.

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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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

Balance, top-loading, readable to 0.01 g, 2000-g capacity

Beakers, Berzelius, tall-form with spout, 200-mL capacity, graduated 25- to 150-mL, borosilicate glass, VWR Scientific, Cat. No. 13922-040, minimum 4 required

Beakers, Griffin, borosilicate glass, graduated, 20-, 400-, and 1000-mL, Fisher Scientific, Cat. Nos. 02-540E, L, and P, respectively

Beaker, Teflon, 250-mL, Fisher Scientific, Cat. No. 02-593-5B

Bottle, glass, amber, narrow mouth, round, 237-mL, with molded plastic, conical polyethylene-lined cap, Fisher Scientific, Cat. No. 02-911-900

Bottle, washing, polyethylene, Right-to-Know Safety Wash Bottles, Distilled Water, 500-mL, Fisher Scientific, Cat. No. 03-409-11E

Brush, scrubbing

Bucket, Nalgene high density polyethylene, 9.5-L capacity, Fisher Scientific, Cat. No. 03-687-30

Buret, weighing, Ace Glass, Cat. No. 9176-02

Calculator or personal computer, with software capable of least squares analysis

Cell, spectrophotometric, 10-mm path length, near-UV glass, rectangular, universally matched, Fisher Scientific, Cat. No. 14-385-910A. Alternatively, a stationary flow cell may be used (see Note 6).

Crucibles, low wide-form porcelain, 30-mL, with cover, Fisher Scientific, Cat. Nos. 07-955E and 07-970G, respectively, several required. Each crucible must be inscribed with an identification number using a hard-tipped scriber. Alternatively, Coors Ceramic marking ink may be used.

Cylinder, graduated, polypropylene, 25-mL, Fisher Scientific, Cat. No. 08-572B

Cylinders, graduated, borosilicate glass, 10-, 25-, 50-, and 500-mL, Fisher Scientific, Cat. Nos. 08-549-5B, C, D, and H, respectively

Filter forceps, stainless steel, Fisher Scientific, Cat. No. 09-753-50

Filtration apparatus, vacuum, borosilicate glass filter holder, 47-mm diameter funnel, 300-mL base with coarse frit support for filter, anodized aluminum spring clamp, Neoprene stopper; vacuum filtering flask, 1-L, Millipore, Cat. Nos. XX10 047-00 and -05, respectively

Flasks, volumetric, Class A, 100-, 200-, 250-, 1000-, and 2000 mL, Fisher Scientific, Cat. Nos. 10-210-5C, D, E, G, and H, respectively

Funnel, filter, 58° angle bowl, short stem, 55-mm diameter, Fisher Scientific, Cat. No. 10-322C

Furnace, programmable, electric, chamber 360-mm wide × 300-mm deep × 330-mm high (minimum), lined with molded refractory ceramic, capable of maintaining $1000 \pm 10^\circ\text{C}$, Fisher Scientific, Cat. No. 10-505-14

Gloves, heavy duty, Fisher Scientific, Cat. No. 11-394-11C

Gloves, nitrile, Fisher Scientific, Cat. No. 19-130-1597, size A to FH

Hot plate stirrer, remote control, adjustable heat and stirrer, ceramic top, heating range to 540°C, Fisher Scientific, Cat. No. 11-675-912Q

Hot plate (non-stirring), Lindberg H-3, Model No. 53015, metal alloy plate surface, heating range 80 to 400°C, VWR Scientific, Cat. No. 33924-402 (optional)

Microwave oven, Ethos EZ, Milestone, Cat. No. 46100, with the following options:

Pressure control, non-contact, QPA0203

Quartz rotor, MRQ01053, includes rotor body, cooling tube, quartz vessels, capping station, stoppers, and rack

Rotor, segmented, SK-10T, includes 10 rotor segments and 10 complete vessels

Rotor, high temperature, HT10400, includes 10 rotor segments, 10 complete vessels, 10 ceramic shields, and temperature sensor

Sensing device, infrared, non-contact, IRT0500

Stirring option, ASM45001

Temperature control for all vessels, TS0000

Temperature probe for rotors, 50214

Pipets, Mohr, 1-, 5-, 10-, and 25-mL, Fisher Scientific, Cat. Nos. 13-665G, K, M, and N, respectively

Pump, vacuum

Scoop, weighing, 20-g capacity, nickel alloy, Fisher Scientific, Cat. No. 01-914-38

Scriber, tungsten carbide pencil, Fisher Scientific, Cat. No. 13-378

Spatula, Fisher scoopula, stainless steel, Fisher Scientific, Cat. No. 14-357

Spectrophotometer, minimum absorbance repeatability of ± 0.0003 at 0.1 Abs, noise less than 0.00005 Abs (rms) at 0.0 Abs, and 0.0006 Abs (rms) at 2.0 Abs, minimum stability of 0.0003 Abs per hour, readability to 0.0001 Abs, Shimadzu, UV-1800 (see *Note 7*)

Standards, absorbance, spectrophotometric, certified, glass filters, 10 to 30% transmittance, 440 to 635 nm wavelength range, National Institute of Standards and Technology (NIST), Cat. No. SRM-2031a

Stirring bars, magnetic, enclosed in Teflon fluorocarbon, 9.5-mm diameter $\times$ 25-mm length, Fisher Scientific, Cat. No. 14-512-128

Thermometer, surface, with temperature probe, Omega Engineering, Cat. Nos. HH81A and 88108K, respectively

Tongs, beaker, Fisher Scientific, Cat. No. 02-622

Watch glass, borosilicate glass, ribbed, 100-mm diameter, Fisher Scientific, Cat. No. 02-613B

Watch glass, PTFE, Fisher Scientific, Cat. No. 02-617-1G

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, except where noted.

Alumina, catalyst support

Catalyst support solution, 40,000 mass/vol-ppm. Prepare in a one-liter beaker by dissolving 40 g of the alumina catalyst support in a solution of 300 mL of water, 250 mL of phosphoric acid and 250 mL of sulfuric acid. After the support has been dissolved by gentle warming, allow the solution to cool to ambient temperature, vacuum filter through a 10.0- μ m filter into a 1000-mL flask. Transfer the filtrate into a 1000-mL volumetric flask and dilute to the mark with water. The solution is stable indefinitely.

Ceramic marking ink, Coors, Fisher Scientific, Cat. No. 11-734 (optional)

Cleaning compound, detergent, Alconox, VWR, Cat. No. 21835-032

Filter, Whatman, glass microfiber, 47-mm diameter, 934-AH, Fisher Scientific, Cat. No. 09-924-451

Filter, Whatman type WCN, 47-mm diameter, 5.0- μ m pore size, 7195-004, Fisher Scientific, Cat. No. 09-905-96

Filters, Teflon membrane, unlaminated, 10.0- μ m, 47-mm diameter, Millipore, Cat. No. LCWP 047 00

Glass beads, 3-mm, solid, borosilicate, Kimble No. 13500-3, Fisher Scientific, Cat. No. 10-310-1. Rinse with water to remove glass chips and allow to dry before use. Alternatively, a small borosilicate glass covered magnetic stirring bar may be used.

Hydrochloric acid, 37%, trace metal grade, Fisher Scientific, Cat. No. A508SK212

Hydrochloric acid solution, 6N, Fisher Scientific, Cat. No. SA56-1, or, prepare by adding 500 mL of concentrated hydrochloric acid measured with a graduated cylinder to an equal volume of water in a 1000-mL volumetric flask and mix.

Hydrofluoric acid, 48-51%, trace metal grade, Fisher Scientific, Cat. No. A513-500

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

Ice, water

Lens paper, optical, Fisher Scientific, Cat. No. 11-996

Microwave mixed acid solution. In a 2-L volumetric flask, combine 720 mL of water with 480 mL of concentrated phosphoric acid and swirl to mix. Add 400 mL of concentrated hydrochloric acid, 20 mL of concentrated nitric acid, and swirl to mix. Allow to cool to room temperature and mix well. Do not dilute to volume.

Mixed acid solution. Prepare in a glass beaker by slowly adding 70 mL of concentrated sulfuric acid to 70 mL of water and allow the mixture to return to room temperature. Add 280 mL of concentrated hydrochloric acid and then pour 70 mL of concentrated phosphoric acid into the acid mixture. The mixed acid solution is stable indefinitely when kept in a stoppered volumetric flask.

Nitric acid, 70%, trace metal grade, Fisher Scientific, Cat. No. A509-212

Phosphoric acid, 85%, Fisher Scientific, Cat. No. AC42404-0025

Pipet, dropping, straight tube, with bulb, Fisher Scientific, Cat. No. 13-701

Platinum standard solution, 1000 mg/L, in 10% hydrochloric acid, SPEX CertiPrep, Cat. No. PLPT3-2X

Stannous chloride, dihydrate, Baker Analyzed Reagent Grade, lot analysis provided, 99.9% minimum purity, Avantor Performance Materials, Cat. No. 3980 (see *Note 8*)

Stannous chloride solution. In a glass beaker, dissolve while stirring 50 ± 0.01 g of the stannous chloride in 50 mL of concentrated hydrochloric acid with gentle warming, if necessary. Transfer the solution to a 100-mL volumetric flask and dilute with water to approximately 95 mL. Allow to cool to ambient temperature, dilute to the mark with water, stopper and mix by inverting several times. Filter the solution through a Whatman glass microfiber filter into a 1-L vacuum filtration flask, using the vacuum filtration apparatus and transfer the solution into another 100-mL volumetric flask. This solution must be prepared daily.

Sulfuric acid, 95-98%, trace metal grade, Fisher Scientific, Cat. No. A510-212

Test paper, potassium iodide-starch, Fisher Scientific, Cat. No. 14-860

Water, deionized or distilled

Wipers, Kimwipes EX-L, laboratory wipers, lint free, Fisher Scientific, Cat. No. 06-666A

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of spectrophotometry, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Platinum Standard Solution

Convert the concentration of the platinum standard solution from mg/L as listed on the certificate of analysis to mg/g as used for calibration, using Equation 1:

$$P = \frac{M}{1000 N} \quad (1)$$

where:

M = concentration of platinum in standard solution, from certificate of analysis, mg/L

N = density of platinum standard solution, from certificate of analysis, g/mL

P = concentration of platinum in standard solution, mg/g

1000 = convert L to mL

Sample Grinding

1. Clean the pulverizer and grind the whole pill catalyst samples as described in UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis."
2. Mix the collected, ground sample thoroughly by randomly shaking it for 5 minutes in an appropriate container.
 - Once the mixing is complete, the homogenous powder must not be agitated again until after the sample is taken.

Preparation of Platinum Working Standards

1. Calculate the volume of catalyst support solution that is required for the matrix match using the Equation 2:

$$X = \frac{2500 W T}{V} \quad (2)$$

where:

T = approximate alumina content of the catalyst to be analyzed, mass fraction

V = final volume of the sample solution for analysis from Table 1, mL

W = mass of catalyst sample to be analyzed from Table 1, g

X = volume of catalyst support solution required for the matrix match, mL

$$2500 = \frac{(10^6)(100)}{40,000} \quad (2a)$$

where:

10^6 = converts g to μg , $\mu\text{g/g}$

100 = final volume of standard solution, mL

$40,000$ = alumina content in catalyst support solution, $\mu\text{g/mL}$

2. Add the volume of catalyst support solution calculated in Step 1 to each of four 200-mL borosilicate beakers using a graduated cylinder.
3. From a weighing buret, transfer aliquots corresponding to 0.7, 1.2 and 1.8 g of the platinum standard solution to three of the 200-mL beakers containing catalyst support solution. Weigh each aliquot to the nearest 0.0001 g.
 - Do not add any platinum solution to the fourth beaker, which will be used to prepare a matrix matched blank.
4. Add a Teflon stirring bar or glass boiling beads to each of the four beakers.
5. Cover each beaker with a ribbed borosilicate watch glass and proceed with Step 1 of *Preparation of Soluble Platinum Species*.

Table 1
Masses of Samples and Volume of Stannous Chloride
Color Developing Solution at Various Pt Contents

Pt Content of Catalyst, mass-%	Catalyst Mass Taken for Analysis, g	Volume of Stannous Chloride Solution for Color Developing, mL	Final Solution Volume for Analysis, mL
0.2	0.8	8	100
0.4	0.4	8	100
0.8	0.4	16	200
1.0	0.4	20	250

Dissolution of gamma-Alumina Catalysts, Using the Hot Plate

1. Weigh, to the nearest 0.0001 g, the appropriate amount of ground catalyst, see Table 1, into a 200-mL borosilicate glass beaker.
 - Take care to deposit the sample mass in one location on the bottom of the beaker.
 - Ground catalysts can be hygroscopic and must be weighed quickly.
2. Weigh duplicate samples into two separate crucibles to determine the LOI at 900°C by UOP Method 954, “Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents,” at the same time that the sample mass is taken for analysis. If the catalyst sample is known to contain potassium, the LOI is determined in duplicate at 700°C.
 - The resultant LOI must be calculated to three significant figures, and duplicates must agree within 5% relative standard deviation.
3. Add 20 mL of the mixed acid solution to the beaker with a graduated cylinder and rinse down any powder adhering to the glass walls with the acid. Add 2 mL of additional mixed acid solution for every 0.1 g of catalyst above 0.4 g.

4. Wet the powder with the acid by gently swirling the acid-powder mixture. Place a Teflon coated stirring bar or glass boiling beads in each beaker.
5. Cover the beaker with a ribbed borosilicate watch glass and make all further reagent additions through the beaker spout to avoid spatter losses.
 - All of the following operations must be performed in a hood.
6. Add 5 mL of hydrogen peroxide and swirl to disperse the sample. Allow the sample to stand for 10 to 15 minutes until chlorine evolution has subsided.
7. Place the covered beaker on a hot plate at ambient temperature in a fume hood. Gradually, over approximately a 15-minute period, increase the temperature of the hot plate to obtain a final surface temperature of $270 \pm 10^\circ\text{C}$.
 - The temperature of the hot plate may be verified with the surface thermometer.
8. Maintain the volume of the solution at approximately 10 to 15 mL by the addition of water as needed.
9. Heat the solution for a minimum of one hour at 270°C until the sample dissolves and all peroxide is removed.
 - Potassium iodide test paper may be used to test the vapors to verify that the hydrogen peroxide has been destroyed.
10. Remove the dissolved sample from the hot plate and allow it to cool, then proceed with Step 1 in *Preparation of Soluble Platinum Species*.

Dissolution of gamma-Alumina Catalysts, Using the Microwave

The ground and homogenized samples are dissolved in closed microwave digestion vessels containing solvent by applying microwave power using specified procedures. The gamma-alumina catalyst samples are digested in the microwave mixed acid solution in Teflon-PFA single-walled or double-walled microwave digestion vessels. The pressure inside the vessel during microwave digestion is monitored and controlled by the pressure controller.

1. Weigh the appropriate amount of ground catalyst (see Table 2) into the bottom of a single-walled, or the liner of a double-walled, microwave digestion vessel. Weigh the catalyst to the nearest 0.0001 g. (See *Notes 1, 2, and 3* for important precautions).

Table 2
Masses of Samples and Volume of Stannous Chloride
Color Developing Solution at Various Platinum Contents

Pt Content of Catalyst, mass-%	Catalyst Mass Taken for Analysis, g	Mass of Platinum Standard Solution Taken, g	Volume of SnCl_2 Solution for Color Developing, mL	Final Solution Volume for Analysis, mL
0.2	0.8	0.5, 1.3, and 2.0	8	100
0.4	0.8	1.0, 2.5, and 4.0	16	200
0.8	0.4	1.0, 2.5, and 4.0	16	200
1.0	0.4	1.3, 3.3, and 5.0	20	250

- UOP Method 918 must be followed for sampling and grinding the whole pill catalyst.
- Since difficulty is experienced in weighing the powdered sample directly into the Teflon vessel/liner due to electrostatic charges, indirect weighing of the sample is recommended. A pretared weighing scoop and spatula may be used for this, if desired.
- Ground catalysts can be hygroscopic and must be weighed quickly.

2. Weigh duplicate samples into two separate crucibles to determine the LOI at 900°C by UOP Method 954, at the same time that the sample mass is taken for sample preparation. If the catalyst sample is known to contain potassium, the LOI is determined in duplicate at 700°C.
 - The resultant LOI must be calculated to three significant figures and duplicates must agree within 5% relative standard deviation.
3. Weigh an amount of alumina catalyst support equal to the amount of catalyst weighed in Step 1 into each of four appropriate microwave digestion vessels.
 - The alumina catalyst support is used to match the matrix in the standard solutions and either fines or spheres may be used.
4. Transfer from a weighing buret, three aliquots of the 1000 mg/L platinum standard solution, corresponding to appropriate amounts as shown in Table 2, into each of three separate microwave digestion vessels that contain the alumina catalyst support. Record the mass of the platinum standard solution added to the nearest 0.0001 g.
 - The vessel containing alumina support with no platinum standard added will be the matrix blank (see *Note 4*).
5. Add 40 ± 1.0 mL of microwave mixed acid solution using a 50-mL graduated cylinder to each of the microwave digestion vessels containing the blank, samples and standards, rinsing the sides of the vessel with the microwave mixed acid solution.
6. Add 40 mL of microwave mixed acid solution to another empty single-walled vessel, fitted with a double port cap for pressure feed back control, or, add 40 mL of microwave mixed acid solution to another double-walled microwave digestion vessel fitted with a cap for pressure feed-back control.
 - Addition of acids should be performed in a fume hood.
7. Place the rupture disk in each single-walled vessel and cap all vessels according to the manufacturer's instructions in the capping station, or, place the rupture membrane in each double-walled microwave digestion vessel and cap according to the manufacturer's instructions.
8. Place the capped vessels in the turntable and connect the vent tubes to each vessel according to the manufacturer's instructions.
9. Place the turntable in the microwave oven.
10. Connect the pressure sensing line to the pressure feed back control vessel according to the manufacturer's instructions for pressure monitoring and controlling.
11. Turn on the microwave oven fan at full speed.
12. Turn on the turntable as per the manufacturer's instructions in the alternating mode.
 - In an alternating mode, the turntable rotates a full turn then reverses direction, so that the pressure sensing line does not become tangled or twisted.
13. Program the microwave oven power to operate at 85% (~510 watts) for 40 minutes when a total of twelve digestion vessels is used, and set the maximum pressure at 520 kPa gauge (75 psig) (see *Note 5*).
 - If the number of digestion vessels is less than 12, reduce the microwave heating time proportionately. For example, when a total of 6 vessels is used, program the microwave oven to operate at 85% (~510 watts) for 20 minutes.
14. Run the program and when it is complete, remove the vessels from the oven and cool them in an ice bucket for 10 minutes.

- Wear insulating gloves to handle the hot vessels.
15. Leave the pressure feed-back control vessel in the microwave oven for approximately 1/2 hour or until the pressure inside the vessel drops to 35 kPa gauge (5 psig). Disconnect the vessel from the pressure sensing line according to the manufacturer's instructions and discard the solution.
 16. After the vessels have cooled to ambient temperature, dry the outer surface of each with a paper towel and uncap them according to the manufacturer's instructions.
 - If there are any signs of venting or sample loss from any microwave digestion vessel, discard that sample and continue with other vessels that have not vented.
 17. Transfer the solutions quantitatively into the appropriate dry and preweighed volumetric flasks, as indicated in Table 2, each containing 40 mL of concentrated HCl for every 200 mL of sample volume. Use 6N HCl for rinsing and keep the volume in the flasks as low as possible.
 - The mass of the dry, empty flask is recorded to the nearest 0.01 g.
 - Although the flasks are equipped with stoppers, the stoppers must not be inserted into the flasks at this point. To avoid errors introduced by weighing volumetric flasks with stoppers that can be mismatched to another flask in a subsequent weighing step, it is recommended that all weighings of volumetric flasks from initial taring to weighing of the final solution volume, be performed without stoppers in place.
 - All solids must be dissolved at this point. Haze or other evidence of undissolved material indicates that dissolution has not been performed properly and must be repeated.
 - If there is a danger of foreign materials falling into the open volumetric flasks, care should be taken to prevent it, for example, by inverting small beakers over the flasks to cover them.
 18. Proceed as indicated in Step 1 in *Color Development*.

Dissolution of theta-Alumina Catalysts, Using the Microwave

The ground and homogenized samples are dissolved in closed microwave digestion vessels containing solvent by applying microwave power using specified procedures. theta-Alumina samples are digested under more vigorous microwave heating conditions employing microwave mixed acid solution, and double-walled microwave digestion vessels must be used. The pressure inside the vessel during microwave digestion is monitored and controlled by the pressure controller.

1. Weigh 0.4 ± 0.01 g of ground catalyst to the nearest 0.0001 g into the liner of a double-walled digestion vessel (See *Notes 1, 2, and 3* for important precautions).
 - UOP Method 918 must be followed for grinding the whole pill catalyst.
 - Since difficulty is experienced in weighing the powdered sample directly into the Teflon liner due to electrostatic charges, indirect weighing of the sample is recommended. A pretared weighing scoop and spatula may be used for this, if desired.
 - Ground catalysts can be hygroscopic and must be weighed quickly.
2. Weigh duplicate samples into two separate crucibles to determine the LOI at 900°C by UOP Method 954, at the same time that the sample mass is taken for sample preparation. If the catalyst sample is known to contain potassium, the LOI is determined in duplicate at 700°C.
 - The resultant LOI must be calculated to three significant figures and duplicates must agree within 5% relative standard deviation.
3. Weigh approximately 0.4 ± 0.01 g of alumina catalyst support (spheres or fines) into each of four double-walled microwave digestion vessel liners.
 - The alumina catalyst support is used to match the matrix in the standard solutions.
4. Transfer from a weighing buret, three aliquots of the platinum standard solution corresponding to approximately 1.0, 2.5 and 4.0 g into each of three separate liners containing the alumina

catalyst support. Record the mass of the platinum standard solution added to the nearest 0.0001 g.

- The alumina support with no platinum standard added will be the matrix blank (see *Note 4*).
5. Add 40 ± 1.0 mL of microwave mixed acid solution using a 50-mL graduated cylinder to each of the digestion vessel liners containing the blank, samples and standards, rinsing the sides of the liner with the microwave mixed acid solution.
 6. Add 40 mL of microwave mixed acid solution to another empty digestion vessel liner and fit the vessel with the adaptor assembly and cap for pressure feed back control.
 - Addition of the microwave mixed acid solution should be performed in a fume hood.
 7. Place the rupture membrane in each vessel and cap all vessels according to the manufacturer's instructions.
 8. Place the capped vessels in the turntable and connect the vent tubes to each vessel according to the manufacturer's instructions.
 9. Place the turntable in the microwave oven.
 10. Connect the pressure sensing line to the pressure feed back control vessel according to the manufacturer's instructions for pressure monitoring and controlling.
 11. Turn on the microwave oven fan at full speed.
 12. Turn on the turntable as per the manufacturer's instructions in the alternating mode.
 - In an alternating mode the turntable rotates a full turn then reverses direction, so that the pressure sensing line does not become tangled or twisted.
 13. Program the microwave oven and pressure controller as shown in Table 3 for a total of twelve double-walled digestion vessels. Set the maximum pressure at 700 kPa gauge (100 psig) (see *Note 5*).

Table 3

Program Level	Power	Time
1P	60% (~360 watts)	1T = 15.00 min
2P	100% (~600 watts)	2T = 30.00 min
3P	100% (~600 watts)	3T = 15.00 min

- If the number of digestion vessels is less than 12, reduce the microwave heating time proportionately. For example, when a total of 6 double-walled vessels is used, use the following program.

1P = 60%	1T = 7.50 min
2P = 100%	2T = 15.00 min
3P = 100%	3T = 7.50 min

14. Continue beginning with Step 14 in *Dissolution of gamma-Alumina Catalysts, Using the Microwave*.

Dissolution of Silica-Alumina Catalysts, Using the Hot Plate

1. Weigh to the nearest 0.0001 g, the appropriate amount of catalyst (see Table 1) into the bottom of a 250-mL Teflon beaker.
 - Since difficulty is experienced in weighing the powdered sample directly into the Teflon beaker due to electrostatic charges, indirect weighing of the sample is recommended. A pretared weighing scoop and a spatula may be used for this, if desired.
 - Take care to deposit the sample mass in one location on the bottom of the beaker.

- Ground catalysts can be hygroscopic and must be weighed quickly.
2. Weigh duplicate samples into two separate crucibles to determine the LOI at 900°C by UOP Method 954 at the same time that the sample mass is taken for analysis.
 - The resultant LOI must be calculated to three significant figures, and duplicates must agree within 5% relative standard deviation.
 3. Rinse down any powder adhering to the Teflon beaker sides with a minimum quantity of water.
 4. Add 10 mL of concentrated sulfuric acid, 5 mL of nitric acid and 10 mL of hydrofluoric acid to the beaker using a plastic graduated cylinder and gently swirl to mix. Cover the beaker with a PTFE watch glass.
 5. Place the covered beaker on a hot plate in a fume hood.
 6. Over approximately 15 minutes, gradually increase the temperature of the hot plate to approximately $270 \pm 10^\circ\text{C}$. Continue to heat the solution until white fumes of sulfur trioxide are first observed, but do not evaporate to dryness.
 - The temperature of the hot plate may be verified with the surface thermometer.
 - The hot plate temperature must not be permitted to exceed 280°C , otherwise significant Pt loss to Teflon occurs.
 7. Remove the beaker from the hot plate and allow it to cool.
 8. Repeat the fuming procedure by adding an additional 5 mL of nitric acid and 10 mL of hydrofluoric acid and repeating the evaporation step.
 9. Repeat the fuming procedure a third time by adding an additional 5 mL of nitric acid and 10 mL of hydrofluoric acid and repeating the evaporation step.
 - At this point, the silica has been removed.
 10. Remove the digested sample from the hot plate and allow it to cool.
 11. Uncover the beaker. Add a Teflon stirring bar or glass boiling beads and 5 mL of 85% phosphoric acid to the beaker, cover it again and proceed with Step 1 in *Preparation of Soluble Platinum Species*.

Preparation of Soluble Platinum Species

1. Add 20 mL of concentrated hydrochloric acid to each beaker including the blank, standards and samples and swirl to mix.
2. Add approximately 2 mL of 30% hydrogen peroxide with a dropping pipet to each beaker through its spout.
3. Allow the solution to stand for approximately 5-10 minutes.
4. Place the beakers on the hot plate which is at a temperature of $270 \pm 10^\circ\text{C}$.
5. Stir slowly if a stirrer-hot plate is used and reduce the solution volume to approximately 25 mL by boiling gently.
6. Continue boiling while periodically adding additional hydrochloric acid to maintain the volume at approximately 25 mL. After thirty minutes of boiling, remove the beakers from the hot plate and allow them to cool.
7. Add approximately 1 mL of 30% hydrogen peroxide and 20 mL of hydrochloric acid to each beaker and swirl to mix the reagents. Allow the solutions to stand for approximately five minutes.

8. Return the beakers to the hot plate and bring them to a gentle boil. Reduce the volume to approximately 25 mL to destroy peroxide and other oxidants.
9. Test one drop of condensate from the underside of the watch glass with a strip of potassium iodide test paper. If it remains white, all traces of oxidizing agents have successfully been removed and proceed directly to Step 11. Otherwise continue with Step 10.
10. Boil the solutions for an additional thirty minutes, maintaining the volume at approximately 25 mL by addition of concentrated hydrochloric acid.
11. Remove the beakers from the hot plate and allow the solutions to cool.
12. Transfer each of the solutions quantitatively into the appropriate, dry volumetric flasks, as indicated in Table 1, after each flask is tared to the nearest 0.01 g. Transfer the blank and the platinum standard solutions quantitatively into separate 100-mL volumetric flasks. Use 6N hydrochloric acid as a wash solution. Keep the volume in the flasks as low as possible.
 - All solids must be totally dissolved at this point. Haze or other evidence of undissolved materials indicates that dissolution has not been performed correctly and must be repeated.
 - The volumetric flask must be weighed and the stopper must not be inserted in the flasks until later. To avoid errors introduced by weighing volumetric flasks with stoppers that can be mismatched to another flask in a subsequent weighing step, it is recommended that all weighings of volumetric flasks from initial taring to weighing of the final solution volume, be performed without stoppers in place.

Color Development

1. Add 8 mL of the stannous chloride solution using a Mohr pipet for every 100 mL of sample volume, as shown in Table 1 (see *Note 8*).
2. Dilute near the mark to a volume of approximately 95 mL with 6N hydrochloric acid. Swirl the flasks but do not stopper until Step 5.
3. Allow the color to develop at a constant temperature for a minimum of 1-1/2 hours.
 - If there is a danger of foreign materials falling into the open volumetric flasks, care should be taken to prevent it, for example, by inverting small beakers over the flasks to cover them.
4. Dilute to the mark with 6N hydrochloric acid and record the final mass of the flask to the nearest 0.01 g.
 - Net mass of the final solution is obtained by subtracting the final mass of the flask with the solution from the mass of the empty flask.
5. Stopper each flask and mix the solution thoroughly by inverting the volumetric flask several times.

Spectrophotometric Measurement of Solutions

1. Calibrate the spectrophotometer once a month at a wavelength of 440 nm with the certified NIST glass filter absorbance standard as outlined in the instrument manual.
 - Spectrophotometers that utilize internal calibration cannot be calibrated with an external standard. In this case, the NIST standard can be used as a performance check.
 - The certified solid standards must be periodically recertified.
2. Adjust the spectrophotometer using the specific instructions supplied by the manufacturer.
3. Zero the spectrophotometer with water at 403 nm in a 10-mm cell in the sample side and air, without a cell, in the reference side.

4. Read the absorbance of the matrix-matched blank, followed by standards and samples at a wavelength of 403 nm (see *Note 6*).
 - It is essential that all color developed solutions be kept at the same constant temperature until the absorbance is read.
 - Once the color is developed, all the samples must be read within approximately 1-2 hours (see *Note 9*).
5. Check the spectrophotometer zero with water to verify that the value remains constant.
 - If the zero is not constant (± 0.001 for a 3 place instrument or ± 0.0003 for a 4 place instrument), repeat the entire measurement sequence as necessary until the initial and final zero and blank readings are constant.
6. Calculate the net absorbance of the standards and samples by subtraction of the matrix blank absorbance using Equation 3:

$$A = B - C \quad (3)$$

where:

A = absorbance of platinum
B = absorbance of sample
C = absorbance of blank

Calculations

1. Calculate the concentrations of platinum in the color developed Pt standards to four significant figures using Equation 4:

$$D = \frac{E F}{G} \quad (4)$$

where:

D = platinum concentration in color developed standard, mg/g
E = mass of platinum standard solution taken, g
F = platinum concentration in standard solution, mg/g
G = total mass of color developed standard solution, g

2. Calculate the best straight line from the three net absorbances of the platinum standard solutions by performing a least squares analysis and obtain the correlation coefficient, *Q*, for the best straight line. Use a calculator or computer capable of least squares analysis.
3. If the value of the correlation coefficient, *Q*, is 0.99986 or greater, the platinum calibration curve is accurate enough for use. If the absolute value of *Q* is less than 0.99986 the calibration has not been performed correctly and must be repeated starting with Step 3 through Step 6 under *Spectrophotometric Measurement of Solutions*.
 - In no case can a two-point calibration, obtained by using the “best” two of the standards, be used for accurate analysis.
4. Calculate the platinum content of the measured sample solution, (*L*) mg/g, by substitution of the platinum absorbance into the algorithm of the calculator or computer used to calculate the best straight line.
5. Calculate the platinum content of the catalyst sample, corrected for loss on ignition, to the nearest 0.0001 mass-% using Equation 5:

$$\text{Pt, mass-\%} = \frac{L S}{10 \left[\frac{J(100 - K)}{100} \right]} \quad (5)$$

where:

- J** = mass of catalyst sample taken for analysis, g
- K** = loss on ignition, mass-%
- L** = platinum content of the sample solution, mg/g
- S** = final mass of color developed solution, g
- 10** = required to convert to mass-%
- 100** = required to convert to mass fraction

Notes and Precautions

1. Never use lined digestion vessels and Teflon PFA vessels simultaneously in the same microwave heating program.
2. The manufacturer's cleaning and inspection guidelines for the microwave digestion vessels must be strictly followed. If the microwave digestion vessels show any signs of stress such as cracks or scratches, they should be immediately discarded.
3. Vessel integrity test: The integrity of microwave vessels (both single- and double-walled) must be evaluated monthly. The test is performed in the following way: 50 mL of water is added to each of twelve microwave vessels using a graduated cylinder. The vessels are capped and sealed following the manufacturer's instructions. The vessels are weighed on an analytical balance and the mass of each vessel is recorded. Following the manufacturer's instructions, the vessels are heated for 30 minutes at 100% (~600 watts) power. After allowing the vessels and vessel contents to cool down to ambient temperature (~1 hr) the vessels are reweighed and the mass differential, if any, is determined. If there is a loss of less than 2.5 g, the vessel integrity is acceptable. Any vessel showing a loss of more than 2.5 g must be taken out of service.
4. The use of a matrix blank is optional, but is recommended as a good laboratory practice.
5. Follow the manufacturer's instructions to check the microwave power delivery monthly.
6. The same cell must be inserted the same way in the light beam each time a measurement is made using air as a reference. Alternatively, a flow-through sample cell, which is never removed from the spectrophotometer, can be used providing conditions are arranged to ensure complete removal of the previous sample each time spectrophotometric data are measured. Proper use of a flow-through cell requires cleaning out between blanks, standards and samples. The cell must first be flushed five times with a 1:1 mixture of concentrated hydrochloric acid and water, followed by five rinses with water. The instrument is then zeroed with water in the sample cell, versus air. Then flush the cell five times with 1:1 hydrochloric acid/water. Follow this with five flushes for each of the blank, standards and samples to a constant absorbance reading, using the next standard or sample solution to rinse out the previous one from the flow cell. After the last sample has been measured, flush the cell with five flushes of 1:1 hydrochloric acid/water, followed by five flushes with water, ending with a recheck of the instrument zero at 403 nm.
7. If the spectrophotometer does not fulfill *all* of the specifications, a spectrophotometer capable of accurate and precise measurement of the absorbance to 3-decimal places (i.e., 0.001 Abs) may be used. But, each absorbance *must* be determined a minimum of 9 times. The nine absorbance readings are then averaged to obtain the absorbance that would be equivalent to that read with a 4-decimal place instrument.
8. Oxidation or hydrolysis of the stannous chloride will render the reagent unusable. The reagent must not be used if it has any yellow color, does not dissolve easily in concentrated hydrochloric acid or has remained more than 6 months in an opened bottle.

9. It is recommended that all analyses be started and completed on the same day. However, if necessary, the analysis may be stopped before the final oxidation step is started. Store the sample in the beaker used for digestion and cover it with an inverted beaker. Resume the analysis by retreating the sample with hydrochloric acid and 30% hydrogen peroxide.

Precision, Hot Plate Dissolution

Site Precision and Reproducibility

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab), and using data collected from each of four laboratories, the within-lab and between-lab estimated standard deviations (esd) were calculated for platinum at the concentrations listed in Table 4. Two tests 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 at the concentrations listed (95% probability). Two tests performed in different laboratories by different analysts, on different days should not differ by more than the reproducibility allowable differences shown in Table 4 at the concentrations listed (95% probability).

Table 4
Site Precision and Reproducibility, mass-%

<u>Sample</u>	<u>Mean</u>	<u>Site Precision</u>		<u>Reproducibility</u>	
		<u>Within-Lab esd</u>	<u>Allowable Difference</u>	<u>Between-Lab esd</u>	<u>Allowable Difference</u>
gamma-alumina	0.28	0.0009	0.003	0.0010	0.003
gamma-alumina	0.25	0.0007	0.002	0.0008	0.003
gamma-alumina	0.75	0.0026	0.007	0.0056	0.009
silica/gamma-alumina	0.31	0.0010	0.003	0.0012	0.004

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.

Precision, Microwave Dissolution

Repeatability, Site Precision, and Reproducibility

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab), and using data collected from each of three laboratories, the within-day, within-lab, and between lab estimated standard deviations (esd) were calculated for platinum at the concentrations listed in Table 5. Two tests 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 5 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 5 at the concentrations listed (95% probability). Two tests performed in different laboratories by different analysts, on different days should not differ by more than the reproducibility allowable differences shown in Table 5 at the concentrations listed (95% probability).

Table 5
Repeatability, Site Precision, and Reproducibility, mass-%

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>		<u>Reproducibility</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>	<u>Between-Lab esd</u>	<u>Allowable Difference</u>
gamma-alumina	0.378	0.0006	0.002	0.0015	0.005	0.0022	0.008
theta-alumina	0.596	0.0007	0.002	0.0023	0.008	0.0032	0.012

The data in Table 5 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.

Time for Analysis

When using hot plate dissolution, the elapsed time for one analysis is 6 hours. The labor requirement is 3 hours. When using microwave dissolution, the approximate elapsed time for one to seven analyses is 6 hours. The labor requirement is 2.5 hours.

Suggested Suppliers

Ace Glass, Inc., 1430 North West Blvd., Vineland, NJ 08362-0688, USA, 1-856-691-3333, www.aceglass.com

Avantor Performance Materials, 3477 Corporate Parkway, Suite #200, Center Valley, PA 18034, USA, 1-610-573-2600, www.avantor materials.com

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

Milestone Inc. 25 Controls Dr. Shelton, CT 06484, USA, 1-866-995-5100, www.milestonesci.com

Millipore, 290 Concord Road, Billerica, MA 01821, USA, 1-978-715-4321, www.millipore .com

National Institute of Standards and Technology (NIST), Standard Reference Materials Group, 100 Bureau Dr., Gaithersburg, MD 20899, USA, 1-301-975-6776, www.nist.gov

Omega Engineering, Inc., Stamford, CT 06907, USA, 1-203-359-1660, www.omega.com

Pyromatics, Inc., 9321 Pineneedle Drive, Mentor, OH 44060, USA, 1-440-352-3500, www.pyromatics.com or www.quartzlabware.com

Shimadzu Scientific Instruments, 7102 Riverwood Dr., Columbia, MD 21046, USA, 1-410-381-1227, www.ssi.shimadzu.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

Whatman, Inc., 800 Centennial Avenue, Piscataway, NJ 08854, USA, 1-800-526-3593 (North America only), www.whatman.com