

PLATINUM IN FRESH PLATINUM-RHENIUM CATALYSTS BY SPECTROPHOTOMETRY

UOP Method 823-90

SCOPE

This method is for determining platinum in fresh gamma-alumina catalysts containing rhenium but not molybdenum. Elements that produce colored ions in the color-development step, such as rhenium, constitute a positive interference, however, compensation for these interfering elements is made with an isoamyl acetate extraction. Concentrations of silica up to approximately 150 ppm do not interfere.

OUTLINE OF METHOD

A sample of the fresh catalyst is ground and treated with hydrochloric, sulfuric and phosphoric acid until all of the alumina is dissolved. Hydrogen peroxide is added to dissolve the platinum. A hydrochloric acid solution of stannous chloride is added to the platinum solution to form a yellow colored complex. A portion of the solution is extracted with isoamyl acetate to remove the platinum-tin color, but leaving rhenium and any other impurities in the aqueous phase. Spectrophotometric measurements are then made of the original and extracted sample solutions at 403 nm. The difference in absorbance is attributable to the platinum content.

The concentration of the platinum is determined by comparing the difference in absorbance to a standard calibration curve prepared from matrix-matched standard platinum solutions. The platinum concentration is corrected to a volatile-free basis by an LOI at 900 C.

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, Berzelius, high form, 200-mL, with spout, borosilicate glass, Fisher Scientific, Cat. No. 02-546B

Bottle, narrow mouth, round, amber glass, 237-mL, with molded plastic conical polyethylene lined cap, Fisher Scientific, Cat. No. 3-320-6C

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Bottle, washing, polyethylene, 500-mL, Fisher Scientific, Cat. No. 03-409-10E

Brush, scrubbing

Buret, weighing, 10-mL, Kimble No. 17200-F10, available from Fisher Scientific

Calculator, capable of least squares analysis, Sharp EL512-T, available from Elek-Tek

Cells, spectrophotometric, 10-mm path length, near-UV glass, rectangular, matched, Fisher Scientific, Cat. No. 14-385-910A

Crucible, high-form, porcelain, 10-mL, Fisher Scientific, Cat. No. 07-965C

Cylinders, graduated, Class A, 25- and 50-mL, Fisher Scientific, Cat. Nos. 08-549-5C and -5D, respectively

Desiccator, with plate, Fisher Scientific, Cat. No. 08-615A

Flask, Kjeldahl, 100-mL, Fisher Scientific, Cat. No. 10-110C

Flasks, volumetric, Class A, 100- and 1000-mL, Fisher Scientific, Cat. Nos. 10-202B and F, respectively

Funnel, filter, 58 degree angle bowl, short stem, 100-mm diameter, Fisher Scientific, Cat. No. 10-322G

Funnel, separatory, Squibb, borosilicate glass, with polyethylene stopper and PTFE-plug stopcock, 60-mL, Fisher Scientific, Cat. No. 10-437-11B

Furnace, programmable, electric, lined with molded refractory ceramic, capable of maintaining 1100 ± 10 C, Fisher Scientific, Cat. No. 10-495A

Hot plate, adjustable heat, ceramic top, Fisher Scientific, Cat. No. 11-495-27

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

Pulverizer, laboratory, capable of grinding catalysts to 0.17-mm (80-mesh or finer), equipped with a stainless steel screen with perforations of 0.61 mm, Hosokawa Micron, Mikro-Samplmill

Spectrophotometer, minimum spectrophotometric accuracy of 0.5% and minimum spectrophotometric repeatability of 0.2%

Standards, absorbance, spectrophotometric, certified, glass filters, 10-30% transmittance, 440 to 635 nm wavelength range, National Institute of Standards and Technology, Cat. No. SRM-930-D

Ultrasonic cleaner, 2.8 L, Fisher Scientific, Cat. No. 15-337-11

Watch glass, plain, borosilicate glass, 65-mm dia., Fisher Scientific, Cat. No. 02-612A

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, except where noted.

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

Acetone, 99% minimum purity (Note 1)

Boiling chips, carborundum, Thomas Scientific, Cat. No. 1590-D33. Boil 25 g of the boiling chips five times with 50 mL of concentrated hydrochloric acid for approximately 10 minutes each time. Decant the acid after each boiling. Rinse the chips with 100-mL portions of water 3 times or until neutral and allow to dry before use.

Catalyst base, gamma-alumina, powder or spheres

Cleaning compound, detergent, Alconox, Fisher Scientific, Cat. No. 04-322-4

Cloths, disposable tissues, paper, Fisher Scientific, Cat. No. 06-666A

Desiccant, indicating Drierite, 8 mesh, Fisher Scientific, Cat. No. 07-578-3A

Digestion acid, prepare by combining 280-mL of concentrated hydrochloric acid, 140-mL of 1:1 sulfuric acid and 70-mL concentrated phosphoric acid. The mixed acid solution is stable indefinitely.

Filter paper, Whatman No. 50, quantitative, hardened, low-ash, 18.5-cm diameter, Fisher Scientific, Cat. No. 09-865G

Glass beads, 3-mm, solid, borosilicate, Kimble Science Products, Cat. No. G6005-1. Rinse with water to remove glass chips and allow to dry before use.

Glass wool, borosilicate glass, Fisher Scientific, Cat. No. 11-388

Hydrochloric acid, concentrated, 37%

Hydrochloric acid, 6-M. Dilute a volume of concentrated hydrochloric acid measured with a graduated cylinder with an equal volume of water. Add the acid to the water and mix.

Hydrochloric acid, 1-M. Dilute one volume of concentrated hydrochloric acid, with nine volumes of water measured with a graduated cylinder and mix. (Used for cleaning glassware, see Note 1)

Hydrogen peroxide, 30%

Isoamyl acetate, 99% minimum purity, Mallinckrodt, Cat. No. 2491

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

Nitric acid, concentrated, 70%

Phosphoric acid, 85%

Platinum wire, 99.99% minimum purity, 0.25-mm (0.01-inch) OD, Aesar, Puratronic 99.99%, Cat. No. 10958

Rhenium solution, 1000 µg/mL rhenium (as perhenate) in water, SPEX, Cat. No. PLRE9-2X

Sample bag, polyethylene, 4-mil thick, 66 cm x 23 cm. Fisher Scientific, Cat. No. 01-816F

Sodium hydroxide, pellets

Sodium hydroxide, approximately 10 mass-%. Dissolve 50 g of sodium hydroxide pellets in approximately 450-mL of water. Prepare only when needed and use, while still warm, from a polyethylene wash bottle for glass cleaning (see Note 1).

Stannous chloride, dihydrate, Baker Analyzed Reagent Grade, lot analysis provided, 99.9% minimum purity, J. T. Baker Chemical, Cat. No. 3980 (See Note 2)

Stannous chloride solution. Dissolve 50 ± 0.01 g of the stannous chloride in 50 mL of concentrated hydrochloric acid with gentle warming if necessary. Allow the solution to cool to ambient temperature if warmed. Filter the solution through a fluted Whatman No. 50 filter into a 100-mL volumetric flask, dilute to the mark with water and mix. Prepare fresh daily.

Sulfuric acid, concentrated, 98%

Sulfuric acid, 1:1. Carefully, and with ice-cooling, pour 500 mL of concentrated sulfuric acid into 500 mL of water, mix and allow to cool.

SAMPLING

Obtain at least 500 mL of a representative fresh catalyst sample. Grind the *entire* sample to a consistency of 0.17-mm (80 mesh) or finer by passing it twice through a laboratory pulverizer equipped with a 0.61-mm (0.024 inch) screen (Note 3). Restrict the production of dust as much as possible and, after grinding, add any powder or dust remaining in the pulverizer to the ground sample. Any unground sample remaining in the pulverizer must be hand ground to pass 80 mesh and added to the sample. Collect the *entire* ground sample and mix it thoroughly in a polyethylene sample bag.

Clean the pulverizer thoroughly after each use by blowing out any small amounts of dust with an air stream and brushing. Take suitable precautions to avoid inhalation of dust. If the sample to be ground is the same type as the previously ground sample, grind and discard approximately 50 mL of the new sample before grinding the portion for analysis. If a different type of catalyst is to be ground, the grinder must be disassembled and cleaned by washing with water and detergent in an ultrasonic cleaner. Clean all exposed parts of the pulverizer by thorough brushing and wiping with paper tissues. The disassembled parts are allowed to dry before the pulverizer is reassembled for the next use. A 50-mL portion of the new type of catalyst is then ground and discarded before the catalyst sample for analysis is collected.

PROCEDURE

Preparation of Standard Platinum Solutions

Standard Platinum Solution

Prepare a standard platinum solution containing 1.0-mg platinum/g as follows:

1. Weigh 1.0 g of clean, dry 99.99% platinum to the nearest 0.1 mg.
2. Transfer the platinum wire quantitatively into a 100-mL Kjeldahl flask.
3. Add 10 mL of concentrated nitric acid and 25-mL of concentrated hydrochloric acid.
 - Treatment of the platinum is conducted at ambient temperature until evolution of chlorine has subsided.
 - The flask must be kept in a fume hood throughout the digestion procedure.
4. Place the solution on a hot plate and heat to a gentle boil.
5. Maintain the solution volume at approximately 30 mL by repeated additions of the mixed acids, in the same proportion as in Step 3, until the platinum wire dissolves.
 - When adding the acids, take care that no solution is lost by spattering.

6. Evaporate the acid solution slowly to a syrup, approximately 3 mL, by gently boiling.
 - It is imperative that the solution does not go to dryness during the volume reduction. Platinum losses will result.
7. Add equal proportions of concentrated hydrochloric acid and hydrogen peroxide dropwise to the evaporating solution and boil gently. Repeat the addition and boil until evolution of the brown nitrogen dioxide fumes ceases.
8. Add 10 mL of concentrated hydrochloric acid and 50 mL of water to the solution.
9. Remove the flask from the hot plate and allow the platinum solution to cool to ambient temperature.
10. Transfer the platinum solution quantitatively to a one-liter volumetric flask, tared to the nearest 0.01 g.
11. Add 15 mL of concentrated hydrochloric acid to the solution.
12. Dilute with water to a mass that will produce a platinum concentration of exactly 1.000-mg platinum per gram of solution, weighed to the nearest 0.01 g.
 - The final mass of the platinum solution is equal to the mass of the platinum wire multiplied by 1000. For example, if 1.0034 g of platinum wire were dissolved, the final mass of the platinum solution would be 1003.40 g.
13. Mix the solution thoroughly by shaking.
14. Subdivide the standard platinum solution, without dilution, into separate 237-mL (or smaller), amber glass bottles and seal with polyethylene lined caps for storage.
 - The stability of the solution in an unopened bottle is not known.
 - Once opened, the standards cannot be used for more than two weeks.

Matrix Matched Platinum Standards

Prepare matrix matched platinum standards as follows:

1. Fill a weighing buret with the standard platinum solution containing 1.0 mg Pt/g and weigh to the nearest 0.1 mg.
2. Transfer 1.2-, 1.5- and 1.8-g aliquots of the solution to three 200-mL high form beakers, respectively, weighted to the nearest 0.1 mg.
 - The platinum contents must span the platinum content expected in the catalyst.
3. Add the appropriate preweighed amount of catalyst base and the pipetted volume of rhenium solution to the solutions in the beakers (see Table 1).
4. Digest the standards as described under *Dissolution*.

Table 1

Sample		Matrix Matched Standards ($\pm 5\%$)		
Estimated Mass-%		Mass for Analysis, g	Catalyst Base, g	Re-Solution (1000 $\mu\text{g/mL}$), mL
Pt	Re			
0.22	0.44	0.700	0.700	3.0
0.40	0.80	0.380	0.380	3.0
0.80	0.25	0.190	0.190	0.5

Sample Analysis**Sample Weighing**

1. Weigh to the nearest 0.1 mg the appropriate amount of fresh ground catalyst into a 200-mL tall form beaker.
 - The sample mass taken for analysis depends on the platinum concentration of the catalyst (see Table 1).
 - Ground samples must be weighed quickly because they can be hygroscopic.
 - The sample is deposited in one location on the bottom of the beaker.
2. Prepare a blank by weighing, to the nearest 0.1 mg, an amount of catalyst base into a 200-mL tall form beaker and adding the appropriate volume of the rhenium solution indicated in Table 1.
 - The mass of catalyst base taken is the same as the sample mass.
3. Weigh duplicate samples into tared crucibles to determine the LOI by UOP 275, heating the powdered sample for 6 hours to achieve constant mass.
 - LOI samples must be weighed at the same time the sample mass is taken for the platinum determination.
4. Calculate the LOI results to 3 significant figures.
 - The duplicates must agree within $\pm 2\%$ relative standard deviation or the LOI's and platinum determination must be repeated.
5. Digest the sample and blank as described under *Dissolution*.

Dissolution

1. Add 25 mL of digestion acid to the blank, sample and standards using a graduated cylinder.
 - Dust adhering to the beaker walls is rinsed down with the acid.
 - Gently swirl the acid to thoroughly wet the powder.
2. Add two boiling chips or glass beads and cover the beaker with a watch glass.
 - Carborundum boiling chips and borosilicate beads can be used interchangeably.
3. Transfer the beaker to a fume hood and add 5 mL of hydrogen peroxide by pipet, through the spout of the beaker.

4. Swirl to mix and allow to stand at room temperature for 10 minutes or until most of the chlorine evolution has subsided.
 - The beaker must be kept in a fume hood until dissolution is complete (Step 13).
5. Place the beaker on a ceramic hot plate and gradually increase the heat to obtain a gentle boil of the acid mixture.
6. Heat the mixture until all of the hydrochloric acid has evaporated.
 - When all of the hydrochloric acid is removed, the solution stops boiling and the volume is approximately 15 mL.
7. Continue to heat until the first white fumes of SO_3 evolve; but *no longer*.
 - All catalyst base should be dissolved with no indication of turbidity.
8. Remove the beaker from the hot plate and allow it to cool to the touch.
 - At this point the samples may be left overnight, if required (Note 4).
9. Rinse the watch glass and the beaker walls with approximately 10 mL of water.
10. Add 30-mL of concentrated hydrochloric acid with a graduated cylinder, one milliliter of hydrogen peroxide by pipet and re-cover the beaker.
11. Swirl the solution gently and allow the beaker to stand until chlorine evolution has subsided, approximately 5 minutes.
12. Return the beaker to the hot plate and gradually bring the mixture to a gentle boil.
13. Continue boiling until the volume is reduced to approximately 20 mL.
14. Remove the beaker from the hot plate and allow the solution to cool.
15. Transfer the solution quantitatively into a 100-mL volumetric flask, using 6-M hydrochloric acid.
 - The boiling chips and any fractured particles are removed by passing the solution through a very small pad of glass wool inserted into the stem of the funnel used to transfer the solutions to the volumetric flask.
16. Dilute to approximately 80 mL with 6-M hydrochloric acid and swirl to mix.

Color Development

1. Add 8-mL of stannous chloride solution to the blank, standards and samples using a Mohr pipet. Stopper the flasks and mix by inverting.
2. Dilute to a volume of approximately 95 mL with 6-M hydrochloric acid and swirl to mix.
3. Allow the color of the standards, samples and blank to develop at the same temperature for 1.5 hours.
4. Dilute to the mark with 6-M hydrochloric acid and thoroughly mix the solutions by inverting the volumetric flasks several times.
5. Designate these solutions, “*Before Extraction*” and *immediately* proceed with *Extraction of the Pt-Sn Complex*.

Extraction of the Pt-Sn Complex

1. Transfer approximately 25-mL of the color developed blank, sample and standard solutions, with a graduated cylinder, into separate, dry, 60-mL separatory funnels.
2. Add 15-mL of isoamyl acetate by pipet to each separatory funnel, stopper and shake for 2 minutes.
3. Allow the liquid phases to completely separate, approximately 2 minutes, and draw off the aqueous lower layer into a second, dry, 60-mL separatory funnel.
 - The isoamyl acetate containing the platinum complex in the first separatory funnel is discarded.
4. Add 15 mL of fresh isoamyl acetate by pipet to the second separatory funnel, stopper and shake for 2 minutes.
5. Allow the two phases to completely separate as before.
6. Drain the lower aqueous phase into a 100-mL volumetric flask and stopper.
 - The second isoamyl acetate layer is discarded.
7. Designate the extracted, aqueous solution collected, “*After Extraction*”.

Spectrophotometric Measurement of Solutions, “Before” and “After” Extraction

1. Calibrate the spectrophotometer once a week at a wavelength of 440 nm using solid, certified standards of known absorbance at that wavelength.
 - Spectrophotometers that are self-calibrating cannot be calibrated with an external standard.
2. Adjust the spectrophotometer using the specific instructions supplied by the manufacturer.
3. Measure the absorbance of each solution against water as reference using a 10-mm cell at a wavelength of 403 nm as follows (Note 5):
 - The absorbance of all the solutions must be measured within one hour of the extraction, and the temperature of all solutions must be the same within one degree C.
4. Zero the spectrophotometer with water.
5. Read the absorbance of the blank before and after extraction.
6. Read the absorbance of each standard or sample solution, before and after extraction.
7. Check the spectrophotometer zero with water and repeat the blank reading to verify that the values are constant within the precision of the instrument.
 - If the blank is not constant (± 0.001 for a 3-place instrument or ± 0.0003 for a 4-place instrument), repeat Steps 4 through 7.
8. Calculate the net platinum absorbance, A , of the standards and samples using the following equation:

$$A = (B - B_B) - (C - C_B) \quad (1)$$

where:

- A** = absorbance of platinum
B = absorbance of sample or standard *Before* extraction
B_B = absorbance of blank, *Before* extraction
C = absorbance of sample or standard *After* extraction
C_B = absorbance of blank, *After* extraction

CALCULATIONS

Spectrophotometer Response

Calculate the best straight line from the three net absorbances (Eq. 1) and the corresponding concentrations of the platinum standard solutions by performing a least squares analysis to obtain the slope, K, intercept, J, and correlation coefficient, Q, to 8 decimal places. Use a calculator capable of least squares analysis or the data reduction system on the spectrophotometer, if available.

If the correlation coefficient, Q, is less than 0.99986, the calibration has not been performed correctly and must be repeated. In no case can a two point calibration, obtained by using the “best” two of the standards, be used.

Platinum in Catalysts

Calculate the platinum content of the measured *sample solution* as follows:

$$L = KA + J \quad (2)$$

where:

- A** = net absorbance of the sample solution (Eq. 1)
J = intercept of least squares fitted equation from calibration curve, previously calculated
K = slope of least squares fitted equation from the standards previously calculated
L = platinum content of the sample solution, mg/mL

Calculate the platinum content of the *catalyst sample* corrected for loss on ignition at 900 C to 0.0001 mass-% as follows:

$$\text{Pt, mass-\%} = \frac{LV}{10 \left(\frac{S(100 - G)}{100} \right)} \quad (3)$$

where:

- G** = loss on ignition at 900 C, mass-%
L = previously calculated (Eq. 2)
S = mass of sample taken for analysis, g
V = volume of color-developed solution, 100 mL
10 = required to convert to mass-%

NOTES AND PRECAUTIONS

1. After an isoamyl acetate extraction, the separatory funnels often contain a thin film of water- and acid-insoluble hydrolized stannous oxide. This can be removed by rinsing with warm caustic, then water, dilute hydrochloric acid and again water. Finally rinse with acetone and allow the separatory funnels to air dry.

2. 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.

3. The pulverizer mill must be checked to verify that it is producing the desired mesh size by periodically grinding a catalyst sample and checking the mesh size by sieving.

4. It is recommended that the analysis of samples be completed within a single day. If necessary, the analysis may be stopped before the color-development step is started. Store the *undiluted* sample in the beaker used for digestion and cover it with an inverted beaker.

5. It is essential that cells used to set the spectrophotometer zero and to measure the absorbance of each standard and each sample are “spectrophotometrically equivalent.” The required “spectrophotometric equivalence” can be attained in a number of ways. For example, the same cell can be inserted in the same way in the light beam each time a measurement is made or the spectrophotometer zero is set. Alternatively, a flow through sample cell, which is never moved from the spectrophotometer, might be used providing conditions are arranged to ensure complete removal of the previous sample each time spectrophotometric data were measured. A third alternative would be to use a set of matched spectrophotometer cells that did not differ within the experimental accuracy of the measurement, i.e., 0.5% of the absorbance.

PRECISION

Repeatability

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 4 laboratories, the within-laboratory estimated standard deviation (esd) was calculated for platinum at the concentrations listed in Table 2. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable difference shown in Table 2 at the concentrations listed (95% probability).

Reproducibility

Two tests performed in different laboratories by different analysts, on different days should not differ by more than the allowable difference shown in Table 2 at the concentrations listed (95% probability).

Table 2

Platinum Concentration, mass-%	Repeatability		Reproducibility	
	Within-Lab esd, mass-%	Allowable Difference, mass-%	Between-Lab esd, mass-%	Allowable Difference, mass-%
0.2159	0.0015	0.004	0.0020	0.008

TIME FOR ANALYSIS

The elapsed time for one analysis is 8 hours. The labor requirement is 6 hours.

REFERENCE

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

SUGGESTED SUPPLIERS

Aesar, 892 Lafayette Rd., P.O. Box 1087, Seabrook, NH 03874-1087
J. T. Baker Chemical Co., 222 Redschool Ln., Phillipsburg, NJ 08865
Elek-Tek, Inc., 6557 N. Lincoln Ave., Chicago, IL 60645
Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143
Hosokawa Micron Div., 10 Chatham Rd., Summit, NJ 07901
Kimble Science Products, Crystal Ave., Vineland, NJ 08360
Mallinckrodt Inc., P.O. Box 5840, St. Louis, MO 63134
National Institute of Standards and Technology, Gaithersburg, MD 20899
SPEX Industries, Inc., 3880 Park Ave., Edison, NJ 08820
Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0090