

PALLADIUM IN CATALYSTS BY VISIBLE SPECTROPHOTOMETRY

UOP Method 592-85

SCOPE

This spectrophotometric method is for determining palladium in alumina or silica-alumina base catalysts and aqueous solutions. The lower limit of detection is about 10 mass-ppm. Other applications are possible if the interference limits are not exceeded.

Cyanide must be absent. Most metals do not present an interference. However, noble metals, such as platinum, rhenium, gold, iridium and ruthenium, can cause up to 3% error when present at ratios above 30:1 relative to palladium.

OUTLINE OF METHOD

The sample is refluxed with concentrated hydrochloric acid and hydrogen peroxide. An aliquot of the dissolved sample or leachate (if sample is not soluble) is reacted with α -furildioxime in a separatory funnel, and the resulting colored complex is extracted with chloroform. The absorbance at 380 nm is measured, and the palladium concentration is calculated based on the absorbance of a standard solution.

APPARATUS

Balance, readability, 0.1-mg

Beakers, 50-mL

Beakers, electrolytic, extra high form, without pour out, 250-mL, Sargent-Welch Scientific, Cat. No. S-4715-B, or equivalent.

Bell jar, high form, with tabulated top opening, 260-mm high by 140-mm diameter, Sargent-Welch Scientific, Cat. No. S-4890A, or equivalent

Cells, spectrophotometer, 10-mm path length, UV Silica, Beckman Instruments Inc., Cat. No. 580012, or equivalent

Condenser, acorn-type (see Fig. 1), UOP Inc., or equivalent. Set up assembly in a fume hood.

Cylinders, graduated, 10- and 25-mL

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Flasks, volumetric, 25-, 100-, 200-, 500-mL and 2-L

Funnel, glass frit support assembly, 47-mm diameter frit, Kontes, Cat. No. K-953750, or equivalent

Funnel, short stem analytical, 35-mm top ID, Sargent-Welch Scientific, Cat. No. S-35309-A, or equivalent

Funnel, separatory, Teflon Stopcock, 125-mL

Hot plate, Sargent-Welch Scientific Co., Cat. No. S-41315, or equivalent

Mortar, porcelain, 130-mm OD, with pestle, Sargent-Welch Scientific, Cat. Nos. S-62250-50 and S-62251-F, respectively, or equivalent

Pipet, dropping, straight tip with bulb, "Medicine Dropper", Sargent-Welch Scientific Co., Cat. No. S-69695, or equivalent.

Pipets, 2-, 5-, 10-, 15- and 20-mL

Spectrophotometer, minimum of $\pm 0.5\%$ photometric accuracy, Beckman Instruments, Inc., Model 35, or equivalent

Vacuum pump, Sargent-Welch Scientific Co., Cat. No. S-71386, or equivalent

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. Unqualified references to solutions mean aqueous solutions.

Boiling chips, carborundum, Thomas Scientific, Cat. No. 1509-D30, or equivalent

Chloroform

Ethanol, absolute, Sargent-Welch Scientific, Cat. No. SC12097, or equivalent

Filter paper, ashless 5.5-cm circles, Whatman No. 40, Fisher Scientific, Cat. No. 09845A, or equivalent

α -Furildioxime, GFS Chemicals, Cat. No. 40802, or equivalent

α -Furildioxime solution. Weigh 1.0818 g $\pm$ 0.5 mg into a 50-mL beaker, add 10 mL of absolute ethanol and apply very low heat with a hot plate until most of the α -furildioxime appears to be in solution. Add 10 mL more of ethanol, carefully rinsing down any solids from the walls of the beaker. Apply low heat again until all the α -furildioxime is in solution and rinse the sides down with 10 mL more of ethanol. Quantitatively transfer to a 100-mL volumetric flask and dilute to volume with water.

Hydrochloric acid, concentrated, 37%

Hydrochloric acid, 2%. Add 4 mL of concentrated hydrochloric acid to a 200-mL volumetric flask containing water. Dilute to volume with water.

Hydrogen peroxide, 30%

Membrane filter disks, 0.22- μ m pore diameter, 47-mm diameter, white, plain, Millipore, Cat. No. GSWP04700, or equivalent

Palladium, powder, 99.999%, Alfa Products, Cat. No. 40052, or equivalent

Palladium stock solution, 350 μ g/mL. Dissolve 0.7000 g $\pm$ 0.1 mg of palladium powder in a 250-mL high form beaker under reflux using the acorn condenser with 50 mL of concentrated hydrochloric acid containing 6 drops of hydrogen peroxide. Add more hydrogen peroxide dropwise throughout the reflux until the metal is dissolved. Reflux 30 minutes after the final addition of hydrogen peroxide. Allow to cool and quantitatively transfer the solution to a 2-liter volumetric flask. Dilute to the mark with water.

Palladium standard solution, 7 μ g/mL. Pipet 10 mL of the palladium stock solution into a 500-mL volumetric flask and dilute to volume with water.

PROCEDURE

Analysis of Catalysts

Grind the catalyst to approximately 80 to 120 mesh with a mortar and pestle. Determine the loss on ignition at 900 C as described in UOP Method 275. Record the mass of the sample before and after ignition and discard the contents of the crucible. Weigh approximately 1.0 g of the ground catalyst to the nearest 0.1 mg into a 250-mL high-form beaker. Add 25 mL of concentrated hydrochloric acid, 6 drops of hydrogen peroxide, and several boiling chips. Using the acorn condenser, reflux in a fume hood until the sample is dissolved, or for 3 hours if the sample is insoluble. If the sample has dissolved, allow it to cool, then quantitatively transfer it to a 200-mL volumetric flask and dilute to volume with water. If the sample has not dissolved, allow it to cool, settle, and then decant the supernatant liquid into a 50-mL beaker. Set the 50-mL beaker and contents aside for further processing. Add 25-mL more of hydrochloric acid and 6 drops of hydrogen peroxide to the 250-mL high-form beaker and reflux for an additional hour. Cool and quantitatively filter this liquid and the previously decanted liquid through a vacuum filtration unit (see Fig. 2), into a 200-mL volumetric flask. Dilute to volume with water. In either case, pipet an aliquot appropriately sized to contain approximately 70 μ g of palladium into a 125-mL separatory funnel. Continue as directed under *Color Development*.

Analysis of Aqueous Solution

Choose a sample quantity that contains approximately 3500 μ g of palladium but do not exceed 75 mL. Weigh the sample to the nearest 0.1 mg into a 250-mL tall-form beaker, add 25 mL of concentrated hydrochloric acid and 6 drops of hydrogen peroxide. Add several boiling chips, reflux 30 minutes, then allow to cool. Quantitatively transfer the solution to a 500-mL volumetric flask and dilute to the mark with water. Pipet an aliquot appropriately sized to contain approximately 70 μ g of palladium into a 125-mL separatory funnel. Continue as directed under *Color Development*.

Color Development

Perform the color development operation in a fume hood. Prepare a reagent blank by pouring 15 mL of 2% hydrochloric acid solution into a 125-mL separatory funnel. Into two other 125-mL separatory funnels, pipet 10-mL aliquots of the 7 μ g/mL palladium standard solution. To these 3 funnels and those containing sample aliquots add 15 mL of 2% hydrochloric acid solution. Pipet 2 mL of the α -furildioxime solution into

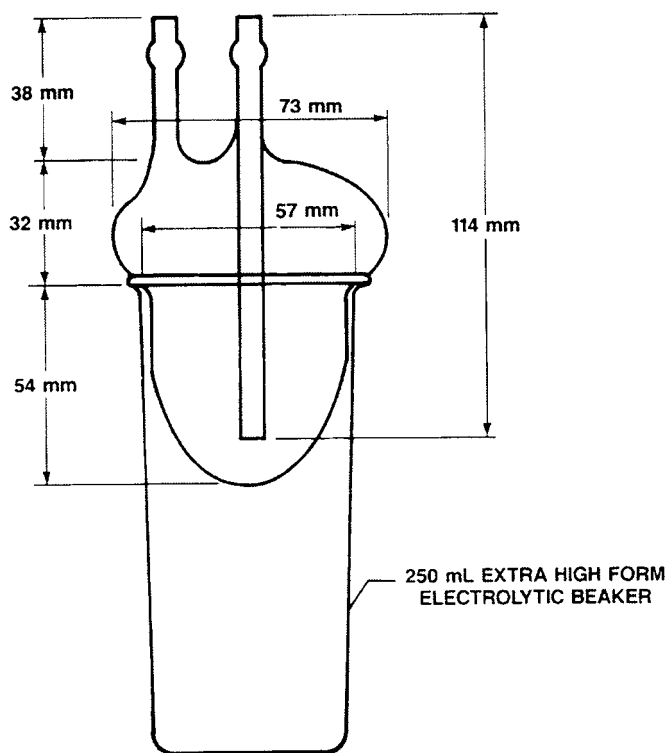


Figure 1
Reflux Vessel

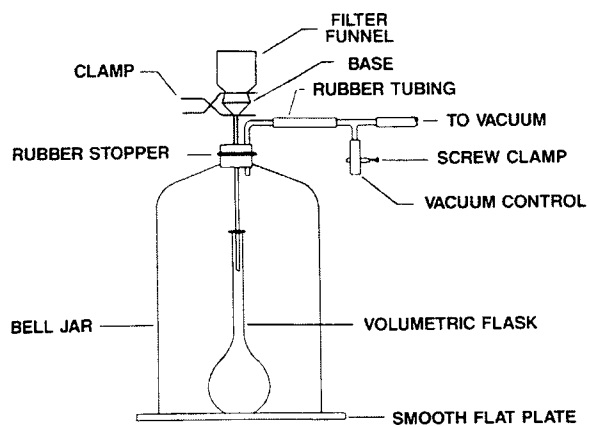


Figure 2
Filtering Apparatus

each funnel and allow to color-develop for 30 minutes. Because the colored complex is not stable for long periods in an aqueous solution, add 5 mL of chloroform to each funnel; shake for 20 seconds, periodically venting the accumulated gases. Allow the layers to separate. Draw off the chloroform (lower) layer, pass it through a 5.5-cm filter circle fitted into a small filter funnel, and collect the filtrate in a 25-mL volumetric flask. To avoid sample losses due to drying of the color complex on the filter paper, rinse the upper edge of the paper several times during filtration by dropwise additions of chloroform from a medicine dropper. Extract the funnel contents two more times with 5-mL portions of chloroform. Again wash the filter paper well with chloroform, collecting the washings in the flask, and dilute to the mark with chloroform.

Read the absorbance of each solution at 380 nm in a 10-mm cell against the reagent blank.

CALCULATIONS

Calculate the concentration of palladium in aqueous solutions or catalyst on an “as received” basis as follows:

$$\text{Palladium, mass-\%} = \frac{100 (70.0) AV}{10^6 SMB}$$

where:

- A** = absorbance of sample solution
- B** = volume of aliquot pipeted from sample solution, mL
- M** = mass of sample taken for analysis, g
- S** = average absorbance of standard solutions
- V** = volume to which digested sample was diluted, mL
- 70.0** = exact mass of palladium in extracted standard aliquot, μg
- 100** = conversion from ratio of palladium mass/sample mass to percent
- 10^6** = conversion from $\mu\text{g/g}$ to g/g

Calculate the concentration of palladium in catalysts on a volatile-free basis as follows:

$$\text{Palladium, volatile-free basis at } 900^\circ\text{C} = \frac{IE}{F}$$

where:

- E** = palladium, as received basis, mass-%
- F** = final mass of sample taken for analysis after ignition at 900°C , g
- I** = initial mass of sample taken for analysis before ignition at 900°C , g

PRECISION

Based on the replicate determinations listed in the table below, the estimated standard deviation (esd) was calculated for different levels and sample types. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Sample type	No. of Replicates	Level mass-%	esd, mass-%	Allowable Difference, mass-%
Acid-soluble	7	0.828	0.0033	0.0114
Acid-soluble	7	0.414	0.0017	0.0058
Acid-insoluble	6	0.490	0.0026	0.0095

TIME FOR ANALYSIS

The elapsed time for an analysis is about 7 hours.

The labor requirement for a group of 4 to 6 samples is 0.75 hour per sample. For a single analysis that is not part of a group, the labor requirement is 1.5 hours.

REFERENCES

Menis, Oscar, and Rains, T.C., *Anal. Chem.* **27**, 1932 (1955)
UOP Method 275

SUGGESTED SUPPLIERS

Alfa Products, P.O. Box 299, 152 Andover Street, Danvers, MA 01923
Beckman Instruments, Inc., Scientific Instruments Division, 2500 Harbor Blvd., Fullerton, CA 92634
Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143
GFS Chemicals, P.O. Box 23214, Columbus, OH 43223
Kontes, P.O. Box 729, Vineland, NJ 08360
Millipore Corporation, Ashby Rd., Bedford, MA 01730
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0090
UOP Inc., Box 5017, Des Plaines, IL 60017-5017