

RHENIUM IN CATALYSTS BY SPECTROPHOTOMETRY

UOP Method 715-85

SCOPE

This method is for determining rhenium in fresh and used platinum-containing catalysts in the range of 0.05 to 0.75%. Elements that produce colored ions in the dissolution or color-development step constitute a positive interference. Iron or copper in moderate concentrations are reduced by stannous ion to a colorless state and, therefore, do not interfere. Molybdenum which forms a red coloration with the stannous ion is the major interference. Directions for the separation of rhenium from molybdenum are given. Analysis for molybdenum is by UOP Method 833.

OUTLINE OF METHOD

A ground, ignited sample of the catalyst is dissolved under reflux with concentrated hydrochloric acid, concentrated phosphoric acid, and 30% hydrogen peroxide. Spectrophotometric measurements are made at 445 nm of the color produced when an aqueous solution of thiourea and a hydrochloric acid solution of stannous chloride are added to the rhenium solution.

APPARATUS

Balance, readability of 0.1-mg

Balance, top-loading, readability 0.1-g

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

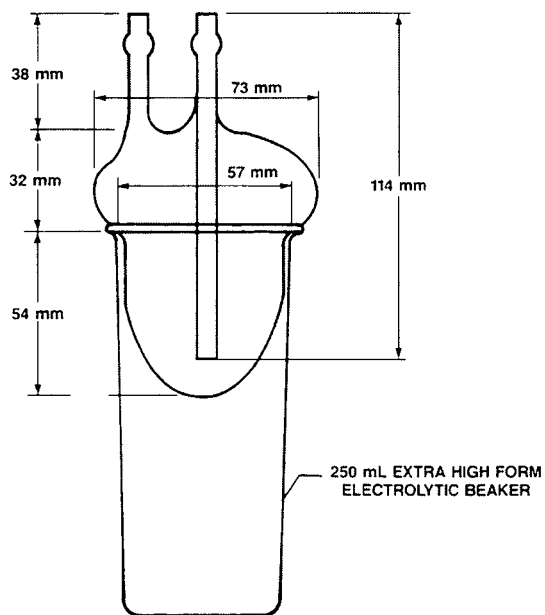
Beakers, Griffin, low form, 250-mL

Beakers, Berzelius, high form, with pour out, 200-mL, Sargent-Welch Scientific, Cat. No. S-4695-D, 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

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).

© COPYRIGHT 1985 UOP LLC
ALL RIGHTS RESERVED

**Figure 1**

Reflux Vessel

Buret, Weighing with Teflon plug stopcock, 10-mL, Sargent-Welch Scientific, Cat. No. S-11107, or equivalent

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

Condenser, acorn type, to fit above beaker (see Fig. 1)

Crucibles, porcelain, Coors 00, with covers

Cylinders, graduated, 25- and 100-mL

Desiccator, with aluminum plate

Flasks, volumetric, 100-, 200- and 2000-mL

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

Funnel, separatory, 250-mL

Furnace, muffle, electric, capable of operation at 900 ± 25 C

Hammer mill, laboratory type, with screen having perforations of 0.61-mm (0.024-inch), Sargent-Welch Scientific, Cat. No. S-60870, or equivalent

Hot plate

Pipets, 5- and 10-mL

Spectrophotometer, minimum of $\pm 0.5\%$ photometric accuracy

Transite, 20-mm thick, 750-mm square, or equivalent, to fit top of hot plate

Watch glass, 75-mm diameter, Sargent-Welch Scientific, Cat. No. S-83605-E, or equivalent

REAGENTS

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.

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

Chloroform

Cupferron, $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$, crystals, Sargent-Welch Scientific, Cat. No. SC17004, or equivalent

Filter paper, Whatman No. 42, Sargent-Welch Scientific, Cat. No. S-33175-F, or equivalent

Hydrochloric acid, concentrated

Hydrochloric acid, 10 vol-%. Add one part concentrated hydrochloric acid to 9 parts water.

Hydrogen peroxide, 30%

Membrane filter disks, 0.22- μm diameter, white, plain, Millipore, Cat. No. GSWP04700, or equivalent

Phosphoric acid, 85%

Rhenium wire, 99.97%, Alfa Products, or equivalent

Stannous chloride. Weigh 25 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ into a 250-mL beaker and add 25 mL of concentrated hydrochloric acid. Warm slightly until solution is complete. Dilute with water to 100 mL. Prepare fresh every other day.

Sulfuric acid, concentrated

Thiourea, 6% aqueous solution. Weigh 12.0 ± 0.1 g of thiourea (Sargent-Welch Scientific, Cat. No. SC-15250, or equivalent) into a 250-mL Griffin beaker. Add 150 mL of water and heat until the solution is complete. Remove from hot plate and allow to cool to room temperature. Filter into a 200-mL volumetric flask through Whatman No. 42 filter paper and dilute to volume. Prepare fresh when solution becomes turbid.

STANDARDIZATION

Preparation of Standard Rhenium Solution

Place $0.36 \text{ g} \pm 0.1 \text{ mg}$ of rhenium wire in a 250-mL electrolytic beaker. Add 2 mL of water and 5 to 7 mL of 30% hydrogen peroxide. Cover with a watch glass. Heat at 85–90 C until the metal is dissolved and then remove the beaker from the hot plate and allow it to cool. Slowly add 25 mL of concentrated hydrochloric acid and gently reflux on a hot plate for two hours. Allow to cool and quantitatively transfer the solution

with water to a clean and dry 2000-mL volumetric flask previously weighed to within 0.1 g. Dilute to the mark with water at room temperature and weigh the flask and contents to within 0.1 g. Determine the mass of the solution by difference. Calculate the titer as follows:

$$\text{Titer, mg of rhenium/g of solution} = \frac{H}{E}$$

where:

E = mass of rhenium solution, g

H = mass of rhenium wire, mg

Determination of Rhenium K Factor

Fill a 10-mL weighing buret with the rhenium standard. Weigh the buret plus contents to the nearest 0.1 mg. Transfer 10 ± 0.1 g of the standard rhenium solution from the weighing buret to a 250-mL electrolytic beaker. Reweigh the buret to the nearest 0.1 mg. To the beaker, add 25 mL of concentrated hydrochloric acid, 5 mL of concentrated phosphoric acid, one milliliter of 30% hydrogen peroxide, and three boiling chips. Place under reflux on a hot plate and continue as directed under *Analysis of Catalyst Containing No Molybdenum* beginning with the paragraph, “When the solution is relatively clear ...”.

PROCEDURE

Determine the molybdenum content by UOP Method 833. If the molybdenum concentration is less than 10% of the expected rhenium content, proceed as described under *Analysis of Catalyst Containing No Molybdenum*. If the molybdenum content is greater than this level, follow the procedure described under *Analysis of Catalyst Containing Molybdenum*.

Analysis of Catalyst Containing No Molybdenum

Grind the catalyst to a consistency of 0.61-mm (0.024-inch) or finer in the hammer mill. Determine the loss on ignition at 900 C as described in UOP Method 275. Record this value and discard the contents of the crucible.

The method is written primarily for catalysts at two rhenium levels, 0.250 and 0.375%, but is not limited to these. For other rhenium levels, adjust the sample mass so that the final color-developed solution contains about 0.018 mg Re/mL. To avoid using sample masses under 0.4 g, choose a sample mass that will yield about 3.6 mg of rhenium when color-developed in a 200-mL volumetric flask.

Place about 0.48 g of the ground sample into a tared Coors crucible and weigh to the nearest 0.1 mg. Determine the mass of the catalyst after ignition at 600 C for one hour on fresh, and 4 hours on used, catalyst. Then determine the loss on ignition at this temperature. Quantitatively transfer the ignited catalyst with water, using caution to prevent loss from dusting, to a 250-mL electrolytic beaker. Add approximately 6 mL of concentrated hydrochloric acid and 6 drops of 30% hydrogen peroxide to the crucible in which the sample was ignited. Allow the crucible to stand for five minutes and transfer the contents to the beaker. Rinse the crucible with three 5-mL portions of concentrated hydrochloric acid, and add this to the contents of the beaker. Then add 5 mL of concentrated phosphoric acid, one milliliter of 30% hydrogen peroxide, and a few boiling chips to the beaker. Reflux on a hot plate to dissolve the sample. See reflux condenser as shown in Fig. 1.

When the solution is relatively clear (1 to 6 hours), allow the contents of the beaker to cool slightly by placing the Transite plate between the beaker and the hot plate. Tilt the beaker slightly and add 4 additional drops of hydrogen peroxide taking care that the drops do not contact the acorn condenser. Continue the reflux for an additional one-half hour.

If samples cannot be completely processed on the same day, discontinue heating, but leave the samples in the reflux apparatus overnight. On the following day, reoxidize the sample by adding 2 to 3 drops hydrogen peroxide, added as indicated in the previous paragraph, and reflux an additional hour.

Allow the dissolved sample or standard to cool until it can be manipulated by hand. Since both fresh and used catalysts may contain insoluble residue, filter the sample as follows:

Set up the filtering apparatus (see Fig. 2). Place a 0.22 μm membrane filter disk on the glass base with the glossy side of the filter facing down. Wet the filter with a small amount of water. Attach the glass funnel and apply vacuum. Quantitatively transfer the solution to a 100-mL volumetric flask through the funnel. Rinse the beaker with three 7-mL portions of 10 vol-% hydrochloric acid, swirling the beaker after each addition. Transfer each of the washings to the funnel. Rinse the filter pad with two 7-mL portions of 10 vol-% hydrochloric acid.

Using a graduated cylinder add 10 mL of thiourea solution and 5 mL of stannous chloride solution to the flask. Mix each solution by swirling the volumetric flask after each addition of the reagents. Dilute the solution to within several milliliters short of the mark with 10 vol-% hydrochloric acid and allow to stand 1-1/2 hours for the color to develop.

Now, dilute the contents of the volumetric flask to the mark with 10 vol-% hydrochloric acid and stopper the flask. Mix the contents by inverting the flask 4 or 5 times. Read the absorbance of the color developed standard or sample against water at 445 nm in 10-mm cells using a minimum slit width.

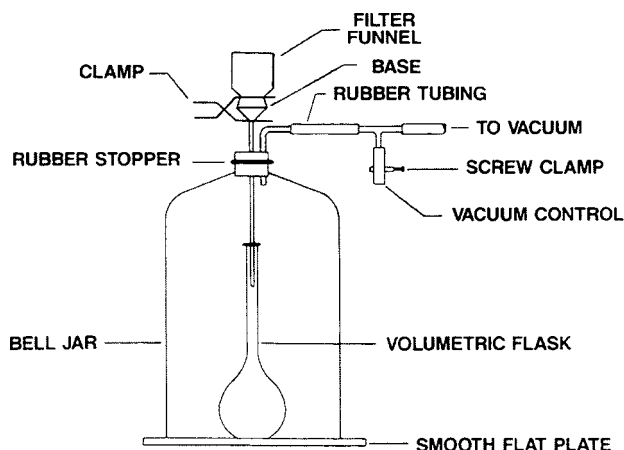


Figure 2

Filtering Apparatus

Analysis of Catalysts Containing Molybdenum

When the molybdenum concentration is greater than 10% of the rhenium content, a separation of the rhenium from the molybdenum is required.

Follow the procedure described for fresh catalyst up to the filtration step. When filtering, collect the filtrate in a 200-mL high form beaker.

Concentrate the filtrate by boiling to a volume of 25 mL, cool in ice water and quantitatively transfer to a 250-mL separatory funnel. Add 10 mL of 20 vol-% sulfuric acid, and then dilute the contents of the separatory funnel to 50 mL with water. The acid and water should also be cooled before addition to the separatory funnel.

Add three 0.35 ± 0.01 g portions of cupferron crystals to the separatory funnel. After each addition extract the solution with 35 mL of chloroform. Shake the contents for two minutes, allow the layers to separate and draw off the lower chloroform layer. After the third extraction, wash the sample with two separate 35-mL portions of chloroform. Discard all chloroform extracts and washings.

Quantitatively transfer the cupferron extracted solution from the separatory funnel to a 200-mL high form beaker. Concentrate by boiling on a hot plate to a volume of 25 mL. Add 15 mL of concentrated hydrochloric acid and 15 drops of 30 vol-% hydrogen peroxide and again concentrate to a volume of 25 mL by boiling. Repeat the additions of hydrochloric acid and hydrogen peroxide followed by concentration to 25 mL until there is no change in the color of the solution. If the solution is cloudy, refilter and then transfer to a 100-mL volumetric flask. Color develop and measure absorbance as described under *Analysis of Catalyst Containing No Molybdenum*.

CALCULATIONS

Determine the rhenium K factor as follows:

$$K = \frac{AT}{CD}$$

where:

- A** = mass of standard rhenium solution, g
- C** = volume of color-developed standard solution, mL
- D** = absorbance of color-developed standard
- K** = mg of rhenium/(absorbance unit)(mL of colored solution)
- T** = titer, previously defined

Calculate the mass-% rhenium in the sample on a 900 C volatile-free basis as follows:

$$\text{Rhenium, mass-}\%, \text{ 900 C volatile-free basis} = \frac{KBV(100 - D)}{10F(100 - E)}$$

where:

- B** = absorbance of color-developed sample
- D** = loss on ignition at 600 C, mass-%
- E** = loss on ignition at 900 C, mass-%
- F** = mass of sample after ignition at 600 C, g
- K** = defined previously
- V** = volume of color-developed solution, mL
- 10** = conversion factor to calculate mass-%, 100/1000 mg/g

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) was calculated for the rhenium levels listed in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Catalyst Type	Rhenium Level, mass-%	esd, mass-%	Allowable Difference, mass-%
Fresh	0.375	0.0009	0.0034
Spent	0.250	0.0009	0.0036

TIME FOR ANALYSIS

The labor requirement is 2 hours per single determination. The elapsed time is 4 hours.

REFERENCES

UOP Method 275

UOP Method 833

SUGGESTED SUPPLIERS

Alfa Products, Thiokol/Ventron Division, 152 Andover St., Danvers, MA 01923

Beckman Instruments, Inc., Scientific Instruments Division, 2500 Harbor Blvd., Fullerton, CA 92634

Kontes, P.O. Box 729, Vineland, NJ 08360

Millipore Corp., Ashby Rd., Bedford, MA 01730

Sargent-Welch Scientific Co., 7300 N. Linder, Skokie, IL 60077

Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0090