

RHENIUM IN PERRHENIC ACID AND AMMONIUM PERRHENATE BY SPECTROPHOTOMETRY

UOP Method 887-89

SCOPE

This method is for determining rhenium in relatively pure perrhenic acid and ammonium perrhenate over a concentration range from 40 to 70 mass-%. Molybdenum is an interference when it is present at concentrations higher than 10% of the rhenium content. Molybdenum can be determined by UOP Method 833. Other elements that produce colored ions in the dissolution or color-development step constitute a positive interference.

OUTLINE OF METHOD

A small quantity of sample is dissolved in or diluted with water and treated with hydrochloric acid and hydrogen peroxide to ensure complete dissolution and oxidation to perrhenate. A suitable aliquot is taken and, after addition of thiourea and stannous chloride in strong hydrochloric acid medium, the lime-yellow color developed is measured spectrophotometrically at 442 nm. The rhenium concentration is determined by comparing the absorbance of the sample to that of rhenium standards that are color developed in the same way as the sample.

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, Mettler AE200, Fisher Scientific, Cat. No. 01-909-405

Balance, top loading, readability 0.01-g, Mettler PM2000, Fisher Scientific, Cat. No. 01-911-174

Beaker, tall form, with spout, graduated, borosilicate glass, 200-mL, Fisher Scientific, Cat. No. 02-546B

Beaker, Griffin type, borosilicate glass, 400-mL, Fisher Scientific, Cat. No. 02-540L

Bottle, glass, 237-mL, narrow mouth, with conical polyethylene screw cap, Fisher Scientific, Cat. No. 03-326-5D

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Bottle, washing, polyethylene, 1000-mL, Fisher Scientific, Cat. No. 03-409-10F

Brush, scrubbing

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

Calculator, capable of least squares analysis, Sharp DL512-T, available from Elek-Tek

Cell, spectrophotometric, matched pair, 10-mm path length, UV-Silica, rectangular, Fisher Scientific, Cat. No. 14-385-910A

Cylinders, graduated, borosilicate glass, 50-, 100- and 250-mL, Fisher Scientific, Cat. Nos. 08-552-4B, C and D, respectively

Flasks, volumetric, Class A, borosilicate glass, with polyethylene stoppers, 100-, 250- and 1000- mL, Fisher Scientific, Cat. Nos. 10-210-5C, E and G, respectively

Forceps, TFE coated tips, Fisher Scientific, Cat. No. 10-317-5

Funnel, filtration, 100-mm top diameter, Fisher Scientific, Cat. No. 10-322G

Hot plate-stirrer combination, Corning PC320, Fisher Scientific, Cat. No. 11-495-29

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

Spatulas, assorted sizes

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

Timer or stopwatch

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

Weighing funnel, Fisher Scientific, Cat. No. 14-353D

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.

Boiling chips, carborundum, Thomas Scientific, Cat. No. 1590-D30. Boil 25 g of the boiling chips 5 times with 50-mL portions 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, using test paper, until neutral and allow to dry before use. Failure to properly wash the chips produces a “haze” in the analytical solutions, which can give erroneous results.

Filter paper, Whatman, No. 50, 18.5-cm diameter, fluted by hand for increased surface area, Fisher Scientific, Cat. No. 09-865-G

Formic acid, 88%, J.T. Baker, Cat. No. 0128

Hydrochloric acid, concentrated, 36.5-38%, J.T. Baker, Cat. No. 9535

Hydrochloric acid solution, 3-M. Dilute 250 mL of concentrated hydrochloric acid to 1000 mL with water and mix. Transfer the acid to a 1000-mL polyethylene wash bottle.

Hydrogen peroxide, 30%, J.T. Baker, Cat. No. 2186

Nitric acid, 69-7.1%, J.T. Baker, Cat. No. 9601

Potassium iodide-starch test paper, Fisher Scientific, Cat. No. 14-860

Rhenium wire, Primary Reference Standard, 50-cm × 0.25-mm diameter, approximately 10 mg/cm, 99.99% minimum purity, Alfa Products, Cat. No. 00276

Stannous chloride, dihydrate, Baker Analyzed Reagent Grade, lot analysis provided, 99.9% minimum purity, J.T. Baker, Cat. No. 3980 (Note 1)

Stannous chloride reagent, 25 mass/vol-%. Weigh 62.5 ± 0.1 g of stannous chloride into a 400- mL beaker, add 62.5 mL of concentrated hydrochloric acid and approximately 100 mL of water. Stir and warm, if necessary, until dissolved. Quantitatively transfer the solution into a 250-mL volumetric flask with water, dilute to volume, mix, and filter through a dry, fluted No. 50 filter paper. Always use freshly prepared solution. The quantity prepared is sufficient for 20-24 samples.

Test paper, pH range 2 through 10, Fisher Scientific, Cat. No. A979

Thiourea, Baker Analyzed Reagent Grade, J.T. Baker, Cat. No. 4123-01

Thiourea reagent, 6 mass/vol-% Weigh 15.0 ± 0.01 g of thiourea into a 400 mL beaker, add about 200 mL of water and stir with a magnetic stirrer until dissolved. Quantitatively transfer the solution into a 250-mL volumetric flask with water and dilute to volume. Mix and filter through a dry, fluted No. 50 filter paper just before use. Prepare fresh daily.

PROCEDURE

Rhenium Standard Solution Preparation

Prepare a 0.5 mg rhenium/g standard solution as follows:

Using TFE tipped forceps, remove the entire 50-cm coil of rhenium-wire (approximately 500 mg) from its plastic envelope and accurately weigh it to the nearest 0.1 mg. Without touching the wire by hand and using only the forceps, place the wire flat on the bottom of a clean, dry 200-mL tall form beaker. From a 50-mL graduated cylinder, add approximately 10 mL of water, two boiling chips, and, using a 10-mL pipet, add 5 mL of concentrated nitric acid. Cover the beaker with a watch glass and keep the watch glass in place throughout the following procedure. Place the beaker on a hot plate at a low heat setting. After the wire has dissolved, approximately 10 to 15 minutes, decompose the excess nitric acid as follows:

Using a one-milliliter pipet add 5 one-milliliter portions of formic acid through the spout of the beaker at 5-minute intervals. Run the solution down the side of the beaker wall. When there is no further evolution of NO_x gases, add an additional 5-mL portion of formic acid using a 10-mL graduated pipet in the same fashion as above. Increase the heat and boil for approximately 15 minutes. Keep the volume above 20 mL by adding small portions of 3-M hydrochloric acid as needed. Determine the volume by comparison to a previously marked beaker.

Add approximately 30-35 mL of concentrated hydrochloric acid. Continue boiling for approximately 15 minutes to remove the excess formic acid. Using a strip of potassium iodidestarch test paper, test a drop of the condensate on the underside of the watch glass, without lifting the watch glass from the beaker. If the paper remains white, all traces of NO_x gases have been successfully removed. If it turns blue, continue boiling the solution, adding 3-M hydrochloric acid to maintain the volume above 20-mL, and retest with fresh potassium iodide-starch test paper until the paper remains white.

Using a one-milliliter pipet, slowly and carefully add two 0.5-mL aliquots of 30% hydrogen peroxide at 5-minute intervals. Boil the solution, maintaining the final volume at 20 mL, by adding 3-M hydrochloric acid. Test the vapors with the potassium iodide-starch paper at intervals until no further peroxide is detected (remains white). The entire rhenium dissolution requires approximately 2 hours.

Allow the solution to cool and quantitatively transfer it with water into a one-liter volumetric flask that has been tared to the nearest 0.01 g. Add 25 mL of concentrated hydrochloric acid and dilute with water to a mass that produces a rhenium concentration of exactly 0.500 mg of rhenium per gram of solution, weighing the solution to the nearest 0.01 g. For example, if 0.5034 g of rhenium wire were dissolved, the final mass of the standard rhenium solution would be 1006.80 g.

This standard solution will be stable for at least two months, but must be subdivided into 237-mL bottles, each of which is sealed with a polyethylene lined cap, properly labeled and dated. Once reopened for use, the standard solution will deteriorate and must not be kept in service for longer than one month.

Sample Preparation

Prepare a solution of the sample as follows:

Solid, Ammonium Perrhenate

Weigh into a weighing funnel to the nearest 0.1 mg approximately 725 mg of sample or, for impure ammonium perrhenate, sufficient sample to contain 500 mg of rhenium. Quantitatively transfer the sample with water into a dry, pre-tared 1000-mL volumetric flask. Add 25 mL of concentrated hydrochloric acid, dissolve and dilute to volume with water. Mix well and re-weigh the flask to the nearest 10 mg.

Aqueous, Perrhenic Acid or Ammonium Perrhenate Liquor

Fill a weighing buret with approximately 5 mL of the liquid sample and weigh it to the nearest 0.1 mg. Estimate the mass of sample solution required to produce 1000 mL of solution having a rhenium concentration of 0.5 mg Re/g. For unknown rhenium solutions, estimate the percent rhenium by multiplying the density by 20. Drain the appropriate mass of sample directly into a dry, pre-tared 1000-mL volumetric flask and re-weigh the weighing buret. To the sample in the volumetric flask, add 25 mL of concentrated hydrochloric acid, swirl to dissolve, dilute to 1000 mL with water and mix well. Reweigh the volumetric flask to the nearest 10 mg.

Analysis of Sample and Standard Solutions

Using the weighing buret, accurately weigh 3.5, 4.0 and 4.5 g of the rhenium standard, and 4.0 g of all sample solutions into 200-mL tall form beakers.

From a 50-mL graduated cylinder, add 50 mL of 3-*M* hydrochloric acid, approximately one milliliter of 30% hydrogen peroxide by pipet and 2 boiling chips. Cover with a watch glass, bring to a boil and evaporate to approximately 20 mL. Also prepare a blank by boiling 50 mL of 3-*M* hydrochloric acid with one milliliter of hydrogen peroxide, and reduce the volume to approximately 20 mL. Make sure all excess hydrogen peroxide has been destroyed by using the potassium iodide-starch paper test described earlier. Allow the solutions to cool.

Color Development and Absorbance Measurement

Quantitatively transfer the solutions to 100-mL volumetric flasks using 3-*M* hydrochloric acid from a wash bottle. Be careful not to exceed a 75-mL total volume by comparing the flask volumes to a reference flask containing 75 mL of water. Using a graduated 10-mL pipet, add to the blank, standard and sample solutions, 10 mL of 6 mass/vol-% thiourea and swirl to mix. Then add by pipet, 10 mL of 25 mass/vol-% stannous chloride reagent. Swirl to mix and allow to stand 90 minutes for color development. When 90 minutes have elapsed, fill the flask to the 100-mL volume with 3-*M* hydrochloric acid from the wash bottle and mix the solution thoroughly by inverting the flask several times.

Calibrate the spectrophotometer once a week at a wavelength of 440 nm using solid, certified standards of known absorbance at the specified wavelength. Adjust the spectrophotometer using the specific instructions supplied by the manufacturer to calibrate the absorbance determined by the instrument.

Measure the absorbance of the colored solutions with the calibrated spectrophotometer using a 10-mm cell at a wavelength of 442 nm as specified below (Note 2). It is essential that all the color-developed solutions be kept at the same constant temperature until the absorbances are read.

Once the color is developed, all the samples must be read within approximately 90-120 minutes (Note 3). Read the absorbance of the standards and sample solutions using the following procedure: First zero the spectrophotometer with water. Then read the absorbance of the matrix matched blank. Then remove the blank and read the absorbance of each standard or sample solution. Check the spectrophotometer zero with water and repeat the blank reading to verify that the values are constant. Repeat the entire measurement sequence as necessary until the initial and final zero and blank readings are constant. Calculate the net absorbance of the standards and samples by subtraction of the blank absorbance (Note 2).

CALCULATIONS

Spectrophotometer Response

Calculate the best straight line from the three net absorbances and the corresponding concentrations of the rhenium standard solutions by performing a least squares analysis to obtain the slope, K ; intercept, J ; and correlation coefficient, Q , for the best straight line. Use a calculator capable of least squares analysis.

If the value of the correlation coefficient, Q , is 0.9999 or greater, the rhenium 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. In no case can a two point calibration, obtained by using the “best” two of the standards, be used for accurate analysis, since discarding one standard greatly decreases accuracy.

Rhenium in Sample

Calculate the rhenium content of the sample solution to the nearest 0.01 mass-% as follows:

$$L = KA + J$$

where:

A = net absorbance of sample solution

J = intercept of least squares fitted equation from the calibration curve, previously calculated

K = slope of least squares fitted equation from the calibration curve, previously calculated

L = rhenium content of the color-developed sample solution, mg

Calculate the rhenium in the original sample to the nearest 0.01 mass-% as follows:

$$\text{Rhenium, mass-\% (as received)} = \frac{LD}{10GW}$$

where:

D = mass of the diluted sample, g

G = mass of the aliquot of sample withdrawn for color development, g

L = previously defined

W = mass of the original sample, g

10 = factor to convert from mg/g to mass-%

NOTES AND PRECAUTIONS

1. Various suppliers of the stannous chloride are satisfactory but care must be exercised when deciding whether a particular batch is acceptable. Occasionally, a usually reliable supplier will deliver impure reagent. The reagent is unacceptable if it contains yellowish discolorations and/or is partially insoluble. In general, if a supplier has previously provided acceptable material, unopened containers of the stannous chloride can probably be used successfully. Once a container is opened, exposure to atmospheric oxygen can slowly degrade the product. Therefore, containers open for more than 4 weeks cannot be used.

2. It is essential that cells used to set the spectrophotometer zero and to measure the absorbance of each standard and sample are spectrophotometrically equivalent. The required 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 can be used if the previous sample is completely removed. A third alternative is to use a set of matched spectrophotometer cells that do not differ by more than the experimental accuracy of the measurement, i.e., 0.5% of the absorbance. Fourth, a single cell may be used with the spectrophotometer zeroed on the blank vs. air.

3. It is recommended that analyses of samples be completed the same day. If necessary, however, the analysis may be stopped before the color-development 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

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 deviations (esd) were calculated at the rhenium concentrations shown in the Table. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences shown in the Table at the concentrations listed (95% probability).

Reproducibility

The between-laboratory estimated standard deviations (esd) were calculated at the rhenium concentrations shown in the Table. Two tests performed in different laboratories by different analysts, on different days, should not differ by more than the allowable differences shown in the Table at the concentrations listed (95% probability).

Table					
Sample Type	Rhenium Concentration, mass-%	Repeatability		Reproducibility	
		Within-Lab esd, mass-%	Allowable Difference, mass-%	Between-Lab esd, mass-%	Allowable Difference, mass-%
Perrhenic Acid	40.71	0.17	0.51	0.26	1.19
Ammonium Perrhenate	69.23	0.34	1.03	0.46	2.08

TIME FOR ANALYSIS

The elapsed time for the analysis of a single sample, not including the preparation of stock solutions, is 8 hours. The labor requirement is 4 hours.

REFERENCE

UOP Method 833, "Molybdenum in Platforming Catalysts and Fines by Atomic Absorption."

SUGGESTED SUPPLIERS

Alfa Products, Thiokol/Ventron Division, 152 Andover St., Danvers, MA 01923
 J.T. Baker Chemical Co., 222 Redschool Ln., Phillipsburg, NJ 08865
 Elek-Tek, 6557 Lincoln Ave., Chicago, IL 60645
 Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143
 National Institute of Standards and Technology, Gaithersburg, MD 20899
 Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085