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The Separation of Rhenium from Copper, Molybdenum, and Tungsten and Its Spectrophotometric Determination

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by

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ABSTRACT

Existing methods for the separation and spectrophotometric determination of rhenium have been modified, applied, and critically evaluated for the determination of rhenium in metal samples containing large amounts of copper, molybdenum, and tungsten. In the method as developed, the rhenium was extracted into chloroform as tetraphenylarsonium perrhenate, following which a color was developed with furil dioxime and measured spectrophotometrically. Many of the ions reported to interfere in the original color method are eliminated here by the chloroform extraction. Copper, molybdenum, tungsten, and hydrofluoric acid may be present in large amounts, and nitrate ion can be tolerated to a lesser degree. In the raffinate from the chloroform extraction, molybdenum and tungsten were analyzed by an existing spectrophotometric procedure. Molybdenum was selectively extracted into pentyl acetate as the dithiol complex from a solution 6N in hydrochloric acid. The absorbance of the complex was measured in the organic solution. In the water phase from this extraction, tungsten was isolated by adjusting the acidity to 9N and reducing the tungsten with titanous chloride. The colored complex of tungsten with dithiol was also extracted into pentyl acetate and measured directly. The analysis of known mixtures of the three metals, containing in addition large amounts of copper, showed recoveries of at least 99% for each, and each had a calculated standard deviation for a single determination of 1%.

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INTRODUCTION

Recently, at this Laboratory, a large number of samples containing copper, rhenium, tungsten, and molybdenum were produced by vapor phase deposition of rhenium, tungsten, and molybdenum on a copper target. The ratios of the individual coating materials were required. A method for tungsten and molybdenum, reported by Nelson and Waterbury (3), was selected, and since they had made an extensive interference study and reported precision data as well, the present effort was concentrated on finding a method for rhenium in the mixture.

Andrew and Gentry (1) described a method which was both rapid and simple. Rhenium was extracted into chloroform as the tetraphenylarsonium complex.and the absorbance was measured directly at 255 millimicrons. We were not able to reproduce their results in the ultraviolet measurement of the absorbance of rhenium. The chloroform extraction, however, worked well, and was retained as the starting point of a procedure. The extraction procedure with tetraphenylarsonium chloride was thoroughly investigated by Tribalat (4), who used the reaction of rhenium with thiocyanate for its eventual determination. The determination of rhenium with this reagent is rather complicated, and a simpler substitute was sought. Meloche, Martin, and Webb (2) reported that furil dioxime formed a colored complex with rhenium(IV) and measured the absorbance at 532 millimicrons in a mixture of water and acetone. The reported interferences included nitrate, fluoride, copper, molybdenum, and palladium.

Our samples contained large amounts of copper and molybdenum, and they required substantial amounts of nitric and hydrofluoric acid for their dissolution. It was necessary, therefore, to ascertain whether the chloroform extraction with tetraphenylarsonium chloride would separate the rhenium in satisfactory fashion. Large amounts of copper, tungsten, molybdenum, and fluoride, and moderate amounts of nitrate were found not to interfere, and it was established that the reaction with furil dioxime provides a sensitive measurement of the amount of rhenium.

EXPERIMENTAL

Since the procedures for molybdenum and tungsten were used essentially as described by Nelson and Waterbury, no further work was necessary except to analyze a series of known mixtures after the rhenium had been removed by chloroform extraction.

Known amounts of rhenium were complexed with tetraphenylarsonium chloride and extracted with chloroform, following the general directions of Andrew and Gentry. In the resulting chloroform solution, the addition of furil dioxime and stannous chloride resulted in the slow formation of a coloration, but the solution was very turbid and the color was not strong. The furil dioxime had been dissolved in acetone as recommended by Meloche, and it was determined that the large amount of acetone exerted a homogenizing influence on the water and chloroform phases. In order to reduce the amount of acetone present, the dye was dissolved in a minimum amount and then diluted with chloroform. Considerable improvement was obtained, but the separated chloroform phase was still somewhat turbid. Centrifuging removed the turbidity in some cases, but not all. It was then found that if the separated chloroform solution was diluted with acetone, a satisfactorily clear solution resulted. A survey of the absorbance spectrum showed maximum absorbance at 532 millimicrons, as found by Meloche and co-workers, and it was established that the absorbance was proportional to the amount of rhenium present.

Known quantities of rhenium were analyzed with no other ions present except some nitric acid which was used to dissolve the rhenium metal in preparing the standard solution. Other portions of the standard were analyzed in the presence of 50 milligrams of hydrofluoric acid and as much as 4 milligrams of copper. No significant differences were seen in the results, but the curve seemed to fall below the straight line with amounts of rhenium greater than 80 micrograms. After a more thorough investigation, it became apparent that the aliquot which contained 80 micrograms of rhenium also contained an amount of nitric acid which began to interfere. Another standard rhenium solution was prepared with less nitric acid, and linearity was obtained as far as was investigated, up to 170 micrograms of rhenium.

The calculated molar absorptivity for the furil dioxime-rhenium complex is 31,000 in the present procedure. This value is considerably less than that found by Meloche for the same complex in a water-acetone medium. However, this sensitivity is quite satisfactory for any ordinary purpose, and the use of a chloroform medium is much more straightforward in the present application.

COLOR DEVELOPMENT

It appears that the color development takes place in the water layer. Both the furil dioxime and the rhenium must pass from the chloroform into the water, where the stannous chloride is available, and the complex is then extracted back into the chloroform. Acetone is observed to speed up the whole process, but too much will homogenize the water and chloroform phases, ruining the determination.

INTERFERENCES

Rhenium

It was established experimentally that above a certain concentration nitrate ion interferes with the rhenium color and causes low results. Up to 400 microliters of 5 percent nitric acid in an aliquot caused no effect in the recommended procedure, and there was only slight interference when 500 microliters were present. Ratios of hydrofluoric acid to rhenium of 1000:1 caused no measurable difference, and ratios of copper to rhenium as high as 100:1 were without effect. Molybdenum and tungsten were each checked at ratios of 40:1 over rhenium and found to produce no detectable interference.

Molybdenum and Tungsten

Nelson and Waterbury commented that nitrate ion is a known interference in the molybdenum and tungsten procedures. It was found experimentally however, that 30 microliters of 5 percent nitric acid did not interfere with the recovery of either molybdenum or tungsten. Tungsten must be in a reduced valence state in order to extract, and large amounts of any oxidizing material will interfere. Excess nitrate ion may be removed by fuming with sulfuric or perchloric acid, but care should be taken to fume the aliquot after the separation of rhenium as it may be volatilized by either of these acids when they are fumed strongly.

CALIBRATION CURVES

Known solutions of each of the metals to be determined must be prepared from pure materials. In the present investigation the solutions of tungsten were prepared by weighing out tungstic acid and dissolving the salt in sodium hydroxide solution. Standard molybdenum solutions were similarly prepared from pure molybdic acid. In the case of rhenium, solutions were prepared by dissolving the spectrographically pure metal in a minimum amount of nitric acid.

The standard solutions are used to prepare sample solutions containing known amounts of each metal. Rhenium should be present in amounts from 30 to 170 micrograms, molybdenum from 5 to 80 micrograms, and tungsten from 10 to 200 micrograms. Each metal is then determined as described in the recommended procedure, and a plot is prepared for each one, showing the measured absorbancies as functions of the concentration. These plots, or factors calculated from them, are then used to convert the absorbance measurements of the samples to micrograms of the metal. The same standard solutions are used to make periodic checks of the performance of the method, and particularly to determine the potency of each dithiol reagent solution.

APPARATUS AND REAGENTS

Apparatus

Beakers, pyrex, 50-ml., and teflon, 60-ml., with teflon covers.

Bottles, polyethylene, 250-ml., with screw caps.

Flasks, Erlenmeyer, 125-ml., with standard taper joints. The matching joint on a 6-in. sealing tube serves as an air condenser.

Flasks, volumetric, assorted sizes.

Funnels, separatory, 60-ml.

pH Meter, Beckman Zeromatic or equivalent.

Pipets, transfer, recalibrated, in assorted sizes.

Spectrophotometer, Beckman Model DU, with 1-cm. absorption cells.

Reagents

Acetone, reagent grade.

Chloroform, reagent grade.

Citric acid, 10% aqueous solution of the reagent grade salt.

Dithiol, 1% solution in pentyl acetate. Break open a 5-gram vial of dithiol (toluene 3-4 dithiol) under pentyl acetate in a stout bottle. Stir to dissolve the dithiol and dilute to 500 ml. with pentyl acetate. Store both the reagent and the solution at -5 to 0°C, and discard the solution if it turns yellow. Each vial of dithiol should be checked by analyzing a known sample of molybdenum or tungsten. The material has shown considerable differences from one vial to the next.

Furil dioxime. The Eastman White Label reagent has been found satisfactory. Prepare the solution each time just before use by weighing out 0.7 gram of the salt and adding 5 ml. of acetone to dissolve. Dilute to 80 ml. with chloroform. If this solution is allowed to stand until the acetone evaporates the reagent will precipitate.

Hydrochloric acid, reagent grade, in 12N, 9.6N, and 6N dilutions.

Hydrofluoric acid, reagent grade, 5% and 48%.

Nitric acid, reagent grade, concentrated.

Pentyl acetate, reagent grade. The Eastman White Label material has been found suitable for use without further treatment.

Potassium permanganate, 1% aqueous solution of the reagent grade salt.

Sodium bicarbonate, 10% aqueous solution of the reagent grade salt.

Sodium hydroxide, 10% aqueous solution of the reagent grade salt.

Stannous chloride, 10% solution. Dissolve 10 grams of the reagent grade salt in 10 ml. of 12N hydrochloric acid and dilute to 100 ml.

Tetraphenylarsonium chloride, 0.1% aqueous solution of the reagent grade salt.

Titanous chloride solution. Dissolve 6 grams of stannous chloride dihydrate in approximately 400 ml. of 12N hydrochloric acid in a 500-ml. borosilicate glass volumetric flask in a well ventilated hood. Cool the solution in an ice bath or in the refrigerator. Cautiously add, while stirring, 5 ml. of titanium tetrachloride. Dilute to volume with concentrated hydrochloric acid and mix well. Storage in the cold will prolong the useful life of the reagent. When the blue color begins to turn brown discard the solution.

RECOMMENDED PROCEDURE

Dissolution of Samples

In a good hood, place the weighed sample in a covered 60-ml. teflon beaker and add 5 ml. of concentrated nitric acid. When the reaction slows, add 1 to 3 ml. of fresh acid. If the vigorous reaction does not resume, add 48% hydrofluoric acid dropwise until dissolution is complete. Moderate heating at the end will help to produce a clear solution. Cool the solution, transfer it to a 200-ml. borosilicate glass volumetric flask, and dilute to volume with water. Mix and transfer as quickly as possible to a polyethylene bottle.

Separation and Determination of Rhenium

Place an aliquot of the sample solution containing 30 to 150 μg. of rhenium in a 50-ml. beaker. Add 0.5 ml. of citric acid solution and 5 to 10 ml. of sodium bicarbonate solution. Adjust the pH to 8 to 9 with sodium hydroxide solution, using the pH meter. Add 2 ml. of tetraphenylarsonium chloride reagent solution and transfer to a 60-ml. separatory funnel. Add 10 ml. of chloroform and shake intermittently for 3 min. Drain the chloroform layer into a second separatory funnel and rinse the aqueous layer with 5 ml. of chloroform, adding it to the first solution. Transfer the aqueous solution, containing the molybdenum and tungsten, to a 25-ml. volumetric flask and reserve it for the determination of those metals.

To the combined chloroform solutions in the separatory funnel, add 3 to 4 ml. of water and 1 drop of dilute permanganate solution, and mix by shaking. Prepare the furil dioxime solution as directed under Reagents, and add 10 ml. of it, followed at once by 10 ml. of stannous chloride solution. Shake the solution intermittently for 5 min. Add 5 ml. of acetone and continue to shake the mixture at intervals until the aqueous layer separates clear. The water will be somewhat yellow, but the turbidity should have disappeared. Place about 5 ml. of acetone in a 50-ml. volumetric flask and drain the chloroform layer from the extraction funnel into it. Rinse the aqueous layer once with 3 to 4 ml.

of chloroform and add it to the flask. Dilute to volume with acetone, mix well, and after 1 hr. measure the absorbance at 532 mμ against a reagent blank. After making any necessary cell corrections, obtain the weight of rhenium present from the calibration curve.

It may be noted that the sensitivity of the method may be increased by diluting the furil dioxime solution to volume with 10% stannous chloride solution rather than with chloroform. This change reduces the volume of the organic layer enough so that it can be placed in a 25-ml. flask for the final dilution. Several low-rhenium samples were handled in this way and later repeated using larger sample aliquots in the usual procedure. There was no difference in the results of the two techniques.

Separation and Determination of Molybdenum

From the solution reserved after the separation of rhenium, take an aliquot containing from 5 to 80 μg. of molybdenum and 10 to 200 μg. of tungsten, and place it in a 60-ml. separatory funnel. Add an equal volume of 12<u>N</u> hydrochloric acid so that the final concentration is 6<u>N</u>. Add 2 drops of 5% hydrofluoric acid, 10 ml. of 6<u>N</u> hydrochloric acid, and 5 ml. of 1% dithiol reagent solution. Shake intermittently for 10 min. and allow the phases to separate. Drain the aqueous layer, which contains the tungsten, into a 125-ml. Erlenmeyer flask. Wash the organic layer twice with 5-ml. portions of 6<u>N</u> hydrochloric acid, adding the liquid to the tungsten solution in the Erlenmeyer flask, and set the solution aside for the determination of tungsten.

Transfer the bright green organic layer to a 25-ml. volumetric flask, rinsing the funnel with more pentyl acetate. Dilute to volume with pentyl acetate, mix thoroughly, and measure the absorbance at 685 mμ using pentyl acetate in the reference cell. Determine the net absorbance by measuring and subtracting a reagent blank, and convert to weight of molybdenum by referring to the calibration curve.

Separation and Determination of Tungsten

To the Erlenmeyer flask containing the solution reserved for tungsten, add 25 ml. of titanous chloride solution and fit the air condenser into place to prevent loss of acid during heating. Heat on the steam bath for 5 to 10 min. and add 10 ml. of 1% dithiol solution. Extract the tungsten by swirling the flask each minute for 20 min. while heating it on the steam bath. Cool to room temperature and transfer to a 60-ml. separatory funnel. Rinse the flask with a minimum amount of pentyl acetate and add it to the funnel. Mixing the phases in the flask just prior to transfer will reduce the amount of pentyl acetate required for rinsing, because the organic layer wets the glass if the transfer is made while the phases are separated. Allow the phases to separate thoroughly, drain off and discard the aqueous phase, and rinse the organic phase twice with 5-ml. portions of 9.6$\underline{N}$ hydrochloric acid, discarding the washings.

Transfer the greenish blue organic layer to a 25-ml. volumetric flask, rinsing the separatory funnel with pentyl acetate. Make up to volume with pentyl acetate and mix thoroughly. Measure the absorbance at 640 mμ, using pentyl acetate in the reference cell. The net absorbance is again obtained by measuring and subtracting a reagent blank at the same wavelength, and the absorbance value is converted to weight of tungsten by referring to the calibration curve.

RELIABILITY

Using the recommended procedure, several series of analyses were made on solutions containing known amounts of rhenium. Based on the results of 21 analyses, in which the rhenium varied from 30 to 170 micrograms, an average recovery of 99.8 percent was found with a standard deviation for a single determination of 1.0 percent. Table I shows the results of the analysis of a series of standards containing varying amounts of nitric acid, molybdenum, tungsten, and copper.

Table I

Recovery of Rhenium in the Presence of Other Ions

HNO_3 (5%), µl.	Mo added, µg.	W added, µg.	Cu added, mg.	Re added, µg.	Re recovered, µg.	Re recovered, %
100			0.8	42.3	42.0	99.3
100			2.0	42.3	43.2	102.1
100			4.0	42.3	42.3	100.0
200	524.	736.	1.0	42.3	42.0	99.3
200	524.	736.	1.0	42.3	41.4	99.0
200			0.8	84.6	85.5	101.1
200			2.0	84.6	84.0	99.3
200			4.0	84.6	84.0	99.3
300	524.	736.	1.0	84.6	84.6	100.0
300	524.	736.	1.0	84.6	83.7	98.9
400			0.8	169.2	168.9	99.8
400				169.2	169.5	100.2

Six of the samples received were prepared by depositing the rhenium, molybdenum, and tungsten on a carefully weighed copper target. The total weight of the deposit was obtained by weighing the finished piece, and this was compared with the sum of the three metals determined by analysis. The six individual recoveries were 99.4%, 96.8%, 100.4%, 98.5%, 98.7%, and 101.1%, giving an average of 99.2%.

SUMMARY

A rapid precise method has been worked out for the determination of rhenium in the presence of copper, molybdenum, tungsten, fluoride, and nitrate. It was applied to samples originating at this Laboratory with satisfactory results. The procedure allows the molybdenum and tungsten to be analyzed after the rhenium has been separated and removed as a possible interference.

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