

Colorimetric Microdetermination of Rhodium with 2-Mercaptobenzoxazole

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A colorimetric procedure has been developed, using 2-mercaptobenzoxazole, for the determination of moderate amounts of rhodium. Interference of iridium is negligible even when present in the proportion of 2 parts to 1 of rhodium. The reactions of other platinum metals are described.

FOR the determination of rhodium, 2-mercaptobenzoxazole has been employed as a colorimetric reagent. The insoluble red mercaptobenzoxazolate of rhodium, which is precipitated from acetic acid medium, is dissolved in acetone to give a yellow-to-red solution, depending on the concentration of the metal. The platinum metals interfering most strongly are platinum and palladium. Iridium and gold in low concentration do not interfere.

Several organic monosulfides have been used for the determination of rhodium. Kienitz and Rombock (4) used thionalide (thioglycollic β -aminonaphthalide) for its volumetric estimation. Currah *et al.* (1) reported the gravimetric determination of rhodium with thiobarbituric acid. The use of 2-mercaptobenzothiazole for the separation of rhodium and palladium from platinum has been reported by Ubaldini and Nebbia (5); 2-mercaptobenzothiazole and 2-mercaptobenzoxazole were used by Haines and Ryan (3) to determine rhodium gravimetrically. In the present investigation the reaction of 2-mercaptobenzoxazole with other platinum metals and the use of this reagent for the colorimetric determination of rhodium have been studied.

REAGENTS

Stock rhodium chloride solution was prepared by dissolving rhodium chloride ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$) in 1 liter of an aqueous solution containing 1 ml. of concentrated hydrochloric acid. This solution, standardized by both the hydrogen sulfide (2) and mercaptobenzoxazole (3) procedures, contained 11.75 mg. of rhodium per 25 ml. of solution. Suitable concentrations were prepared as needed by diluting the stock solution with water.

Solutions of platinum, palladium, iridium, and gold were prepared by dissolving the pure metal or a suitable pure salt in aqua regia, hydrochloric acid, or water, removing nitric acid, if present, by evaporating to dryness in the presence of hydrochloric acid, and finally dissolving in a solution containing 1 ml. of concentrated hydrochloric acid per liter.

2-Mercaptobenzoxazole solution was made by dissolving 1 gram of the reagent (obtained from Eastman Kodak Company) in 100 ml. of 95% ethyl alcohol.

DEVELOPMENT OF METHOD

During the investigation of five organic mercapto compounds, it was found that rhodium could be precipitated quantitatively with 2-mercaptobenzoxazole or 2-mercaptobenzothiazole. Subsequent investigation indicated that these reagents might show colorimetric possibilities. It was found that the red 2-mercaptobenzoxazolate dissolved in acetone to give a colored solution suitable for the determination of rhodium; the 2-mercaptobenzothiazolate proved to be only partially soluble in acetone. The transmittancy curve for acetone solution of the rhodium compound is given in Figure 1.

The data for this curve were obtained with a Model DU Beckman spectrophotometer using a 1-cm. cell. The compound curve was obtained for a solution containing 24 micrograms of rhodium prepared in the same manner as for the colorimetric determina-

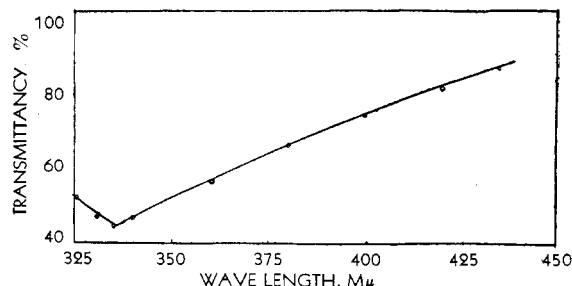


Figure 1. Transmittancy of Rhodium in Acetone Solution

tion. Although maximum absorption occurs in the ultraviolet, good results are obtained using a blue filter. All reported results were obtained using a blue filter (maximum transmittancy at 420 mμ) with a Lumetron photoelectric colorimeter, Model 400A, and voltage stabilizer.

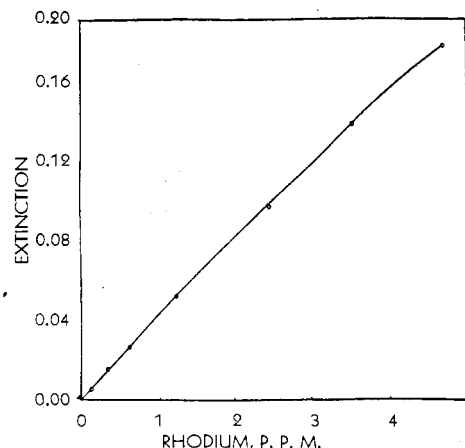


Figure 2. Determination of Rhodium

PROCEDURE

The following method may be applied in the determination of 0.01 to 1.0 mg. of rhodium.

Rhodium samples were measured into Erlenmeyer flasks fitted with short-stemmed funnels, 1 to 2 ml. of concentrated acetic acid and a few drops of the reagent were added, and the volume was made up to approximately 20 ml. The solutions were allowed to boil vigorously on a hot plate for 15 minutes and, after cooling to room temperature, the precipitates were separated from the 2 to 3 ml. of solution remaining by drawing off the supernatant liquid with a filter stick or by filtering directly through a fine filter crucible. The precipitates were dissolved in acetone, the volume was made up to 100 ml., and extinction was measured with colorimeter. A straight-line relationship is not obtained, denoting nonconformity to Beer's law (see Figure 2).

In order to obtain reliable results the solutions must be boiled vigorously for 15 minutes, so that complete precipitation of the

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rhodium is obtained. The acetone solution is stable, no perceptible change in color intensity being noted in 4 days.

REACTION OF 2-MERCAPTOBENZOXAZOLE WITH OTHER PLATINUM METALS

Under the same conditions of precipitation as with rhodium, Pt⁺⁺⁺⁺, Pd⁺⁺, Ir⁺⁺⁺⁺, and Au⁺⁺⁺ give precipitates with 2-mercaptobenzoxazole. The reactions shown below were obtained using 5 mg. of the platinum metal in 25 ml. of solution.

Platinum. Immediate chocolate-brown precipitate changing to brownish yellow on heating; partially soluble in acetone.

Palladium. Immediate red precipitate changing to orange yellow on heating; partially soluble in acetone.

Iridium. Slight brownish red precipitate on heating; partially soluble in acetone.

Rhodium. Red precipitate on heating; readily soluble in acetone.

Gold. Purple-brown precipitate changing to light brown on heating; insoluble in acetone.

INTERFERENCE OF PLATINUM METALS

The platinum metals interfering most strongly are platinum and palladium. Iridium in low concentrations does not interfere. Large quantities of gold cause no interference, because the gold precipitate is insoluble in acetone. Table I shows typical results in the colorimetric determination of rhodium with 2-mercaptobenzoxazole.

The noninterference of iridium in at least equivalent amounts is particularly noteworthy, for rhodium is usually left with this element in the systematic analysis of the platinum group metals (2).

Solvents. Hexane, benzene, ethyl ether, methanol, ethanol, and carbon tetrachloride do not dissolve the mercaptobenzoxazole. Methyl ethyl ketone and dioxane, although readily dissolving the rhodium precipitate, show no advantages over acetone.

Water in Acetone. Measurements of the extinction (at 420 m μ) of solutions varying from 1 to 30% in water were the same. Beyond this limit difficulty is encountered due to complex pre-

Table I. Determination of Rhodium with 2-Mercaptobenzoxazole

(Final volume 100 ml. Extinction measured using blue filter with Lumetron Model 400A)

Rh Present, γ	Rh Found, γ
12	11
25	26
60	58
120	120
94 + 120 γ Pt	116
94 + 140 γ Pd	150
94 + 0.5 mg. Au	94
94 + 1.0 mg. Au	96
94 + 50 γ Ir	92
94 + 100 γ Ir	89
94 + 200 γ Ir	94
940 + 1.5 mg. Ir	937

cipitating out of solution; precipitates appear if more than 35% water is present.

Reagent Solution. The reagent is stable for at least 2 weeks. If reagent solution is allowed to stand, the rhodium precipitate obtained proves difficultly soluble in acetone. Complete transmittancy is obtained beyond 360 m μ for 10 mg. of the reagent in 100 ml. of acetone and excess reagent causes no interference.

Excess Acid. Variations in the acetic acid concentration from 1 to 30%, in the precipitation of the complex, showed no change in the extinction obtained.

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Fractional Sublimation on a Removable Transparent Film

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An apparatus is described for separating the components of a mixture of organic compounds by sublimation at reduced pressure. The sublimate is deposited on a removable transparent plastic film. Microscopic examination of the sublimate as well as chemical tests thereon may be performed without removing the sublimate from the film.

SUBLIMATION procedures have long been recognized as a means for separating and purifying those organic compounds which may, upon heating, undergo direct transition from the solid to the gaseous phase without decomposition. The number of sublimable compounds has been greatly increased by the use of reduced pressure. The advantages of sublimation over other methods of purification have been adequately discussed by Hubacher (2).

Many sublimation apparatus and techniques have been described (2), in which the sublimate is usually collected on the surface of a glass receiver. In order to perform subsequent chemical or microscopical tests, the crystalline sublimate must be removed either by a scraping process or by dissolution in a suitable solvent. If a scraping procedure is employed, the more or less well formed crystals are likely to be damaged. If two or more components of a mixture have been fractionally

separated by a single sublimation, a subsequent dissolution procedure will obviously defeat the original purpose of the sublimation.

To overcome this difficulty, a procedure was devised whereby the sublimed crystals, without further manipulation, may be examined directly on the collecting surface. A sublimation tube consisting of two cylindrical sections connected by a ground-glass joint was designed and constructed as shown in Figure 1. The male ground-glass joint is of constant diameter throughout its entire length and has exactly the same diameter as the rest of the tubing to which it is connected. This feature eliminates the dead space at the joint usually found in the standard type of ground-glass joints. The use of this straight-walled sublimation tube permits the insertion of a transparent cellophane film (which serves as a condensing surface for the sublimate) without the presence of any dead space between the film and inner wall