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THE DETERMINATION OF RUTHENIUM IN URANIUM

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THE DETERMINATION OF RUTHENIUM IN URANIUM

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Introduction

Recently the need arose for the determination of non-radioactive ruthenium in uranium solutions which contained molybdenum and ruthenium in approximately equal concentrations. These concentrations ranged from 25 $\mu\text{g/ml}$ to 150 $\mu\text{g/ml}$, making gravimetric determinations impractical. Colorimetric procedures were investigated and the thiocyanate complex seemed most feasible (1). Since thiocyanate also complexes molybdenum, uranium and various other elements, the ruthenium had to be satisfactorily separated from these interfering elements.

The distillation of radioactive ruthenium from a perchloric acid medium, has been satisfactorily accomplished by Dr. B. F. Rider, Chemistry/Chemical-Engineering Section and others (2). The ruthenium is oxidized to the tetroxide and collected in caustic as the ruthenate (3). Phosphoric acid in the distillate prevents the evolution of molybdenum and sodium bisulfate oxidizes halogens to their non-volatile oxy-acids. The thiocyanate complex is then developed from the ruthenate without interference from other complex forming elements.

Procedure

A 50 ml distillation flask, designed by C. F. Pachucki in 1950 for the distillation of radioactive ruthenium, was used. It is designed so the addition tube is below the level of the distillate. The delivery tube was immersed in 10 ml of 0.1N KOH at 0°C. To the flask was added: 0.5g of NaBiO_3 , sample, 1 ml of 85% H_3PO_4 and 10 ml of 70% HClO_4 . Air was bubbled through the distillate by means of a line attached to the addition tube, at the rate of 2 to 4 bubbles per second. Heat was applied to the flask by means of a heating

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mantle, and the distillation was carried until the brown color of the distillant disappeared and a few drops of the HClO_4 distilled over.

The receiver, a 50 ml volumetric flask, was removed and to it was added 0.5 ml of conc. HCl . The solution was mixed, let stand 3 minutes and then 10 ml of glacial acetic acid and 10 ml of 95% ethanol was added. Seven ml of 25% KCNS was then added and the flask was heated at 85°C for 40 minutes in a hot water bath. After the flask was cooled to room temperature and diluted to the mark with 95% ethanol, the color was read at 565 $\text{m}\mu$ through a 2.5 cm cell on a model B Beckman spectrophotometer.

Experimental and Discussion

Other distillation procedures (4), such as those using $\text{H}_2\text{SO}_4\text{-NaBrO}_3$, are satisfactory but require 2 hours as compared with 20 minutes for the $\text{HClO}_4\text{-NaBiO}_3$ distillation. The HClO_4 distillation was originated for radioactive ruthenium, using RuCl_3 as carrier, after which the ruthenium is reduced to the metal and counted giving a range of recovery from 94.5% to 97.4% (2). In the presence of radioactivity, KI can be added to the distillant, as a hold-back carrier, for any radioactive iodine present might increase the ruthenium count.

The ruthenium is oxidized from the lower oxidation states to RuO_4 during the distillation and is reduced to K_2RuO_4 (ruthenate) in the receiver. If the mole ratio of RuO_4 to KOH is such that the RuO_4 exceeds the KOH , the K_2RuO_4 will disassociate (6) to KRuO_4 (perruthenate) and RuO_2 .

The ruthenate is presumably reduced to the ruthenichlorides (5), K_2RuCl_6 and $\text{K}_2\text{RuCl}_5\text{OH}$ upon the addition of the HCl . It was found that 0.5 ml of HCl gave the most complete and most reproducible oxidation state adjustment and a time of 3 minutes was quite critical. Other reducing agents such as SnCl_2 ,

iron and hydroxylamine hydrochloride were used but the results obtained were no better and in most cases not as good as with HCl-ethanol. The oxidation state was further adjusted by the addition of acetic acid and ethanol, and the violet thiocyanate complex color was developed by heating.

The observed thiocyanate color was scanned (Fig. I) on a General Electric Recording Spectrophotometer and the minimum was found at 565 $m\mu$ to 575 $m\mu$, corresponding to that previously observed (1). Figure II shows the percent transmission at 565 $m\mu$ as a function of ruthenium concentrations under various conditions. Ruthenium trichloride was used for the standard calibration curve. It was dissolved in approximately 0.2N HCl at the concentration of 0.1 mg/ml. Appropriate additions were used to obtain the desired amounts of ruthenium in the standard solutions. The thiocyanate color was developed merely by adding the standard, acetic acid, ethanol, KCNS and heating for 40 minutes at 85°C. The curve of ruthenium distillation was obtained by distilling the same standard amounts of ruthenium from $HClO_4$ as described above. The curves for standard calibration and distilled ruthenium (Fig. II) were plotted from the data in Table I.

Table I

Ruthenium Thiocyanate Complex Color Development of Non-Distilled and Distilled Standards at 565 $m\mu$

<u>mg Ru</u>	<u>Nondistilled % Transmission</u>	<u>Distilled % Transmission</u>
0.1	65.8	59.2
0.2	43.4	51.5
0.3	27.8	39.2
0.4	17.6	26.7

The percent transmission is reproducible with good technique, to $\pm 2\%$ transmission ($\pm 5\%$ ruthenium concentration). The heating time is critical up to about 30 minutes (1) so, to insure maximum color development, the samples

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were heated 40 minutes.

When the thiocyanate complex is developed from the KOH without adding HCl, the color is purple instead of violet and fades completely or to a light blue after 25 minutes of heating. Water and 0.1N HCl were substituted for KOH in the receiver and the colors developed were purple and violet respectively. They both held for 40 minutes at 85°C but the reproducibility was very poor. The percent recovery ranged from 58.5% to 95.5% for H₂O and from 45.0% to 75.0% for 0.1N HCl.

The ruthenium percent recovery for the procedure as written holds at 78% ± 5% as can be calculated from Table 1, for the range examined. A number of samples containing two grams of uranium and known additions of ruthenium were analyzed for ruthenium by the distillation procedure. The results obtained were the same as those containing no uranium. Also molybdenum added to similar samples prior to distillation did not interfere in the ruthenium determination.

Conclusion

This procedure has possibilities as a service analytical procedure but probably could be improved as to the percent recovery. The main trouble does not appear to be the distillation step but rather adjusting the oxidation states of ruthenium. The RuIII oxidation state is the most stable (3) but reducing from the VI and VII states reproducibly seems to be a problem worth further investigation.

There also is the possibility of analyzing ruthenium polarographically or electrometrically reducing the ruthenium to the desired oxidation state.

Acknowledgment

The help of Chester F. Pachucki in performing numerous distillations is appreciated.

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FIG. I ABSORPTION BY RUTHENIUM THIOCYANATE COMPLEX

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TRANSMITTANCE (PERCENT)

TEST NO. BY

DATE

GENERAL ELECTRIC
RECORDING SPECTROPHOTOMETER

INSTRUMENT NO.

1-12-55
L. Yeller

789-28

WAVELENGTH IN MILLIMICRONS

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Fig. II - Calibration Curves for Ruthenium Thiocyanate
at 565 mμ (2.5 cm cells)

1 Cycle x 10 Divisions Per Inch

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■ Non-distilled
○ Distilled

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