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Chemistry - Radiation and Radiochemistry

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PRECIPITATION OF RADIORUTHENIUM

by

F. E. Butler
Health Physics Section
Savannah River Plant

June 1960

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ABSTRACT

Radioruthenium sulfides were quantitatively precipitated from solutions containing any one of five reagents. A procedure is described for the specific determination of ruthenium in an acid solution of mixed fission products and induced activities.

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PRECIPITATION OF RADIORUTHENIUM

INTRODUCTION

An accurate, reproducible method was needed for routine analysis of radioruthenium in environmental samples. Complete and specific separation of ruthenium has been a problem in the analysis of both the natural and the radioactive species because ruthenium exists in multiple valence states and nearly always occurs with chemically similar elements. Accurate assay of radioruthenium is complicated by the problem of separating it from relatively large amounts of other fission products. The nuclide may also be a contaminant in other specific analyses unless it is adequately removed from the mixture.

Health Physics environmental monitoring at the Savannah River Plant includes determination of radionuclides in air filters, soils, sediments, vegetation, and water samples. Samples are leached or ashed and then prepared in acid solutions. Ruthenium is determined first in these acid solutions.

The method previously used by the Health Physics laboratory was based on oxidation of ruthenium to the volatile tetroxide. This procedure was time consuming for routine analysis and produced inconsistent recoveries.

SUMMARY

A simple procedure was developed for the complete and specific separation of radioruthenium in a form suitable for routine radioassay techniques.

Five precipitating agents for radioruthenium were evaluated: thioacetamide, thiourea, thiophenol, β-mercaptopropionic acid, and 2,3-dimercaptopropanal. The precipitates formed are classified as simple or complex sulfides. Approximately 97% recovery of Ru^{103} and Ru^{106} tracers was obtained with thioacetamide and thiourea in dilute HCl solutions, although an average recovery of 94% was obtained with all of the reagents in fission product mixtures whose normalities ranged from 5N in HCl to 6N in NaOH. Decontamination factors for other fission products and for other radioisotopes were approximately 1000. A group of eight samples can be prepared for counting in one hour.

DISCUSSION

SUMMARY OF PREVIOUS ANALYTICAL METHODS

Previous methods for analysis of ruthenium fall into one or more of six general categories. Since many bibliographies are available on the subject, only a few references are given here:

Complexing Agents(1,2,3)

Many analytical methods use reagents that react with ruthenium. The emphasis has been on spectrophotometric comparison of colored solutions with standards. No reference was concerned with a simple quantitative laboratory precipitation followed by a counting technique. Several references, however, did suggest the precipitants used in this procedure.

Ion Exchange and Chromatography(4,5,6)

Ruthenium separation by these methods is not quantitative.

Distillation as Ruthenium Tetroxide(7)

Ruthenium forms the volatile tetroxide, which can be absorbed, precipitated, and counted. This method requires much time and a large amount of equipment, and involves the use of hazardous oxidizing agents.

Gamma Spectrometry(8)

In the presence of other fission products this method is qualitative at best unless exacting calibration standards are established and the ratio of Ru^{103} to Ru^{106} is known.

Electrodeposition(9)

The method is not sufficiently sensitive for laboratory quantities of radioruthenium.

Extraction(10)

No specific extractant is available.

EXPERIMENTAL

Precipitation of ruthenium as the sulfide proved to be most promising. The reagents were either mercaptans or compounds that tautomerized to mercaptans in solutions. A satisfactory procedure was developed with thioacetamide, thiourea, thiophenol, β-mercaptopropionic acid (B-MPA), and 2,3-dimercaptopropanal-1 (BAL). P-toluenethiol, mercaptosuccinic acid, and thiobenzanilide showed little promise during initial experiments and were not investigated further.

The following procedure, which was tested with synthetic solutions containing radioruthenium and other nuclides, is recommended for general analytical use:

1. Prepare the solution to 2-3 normal in HNO_3 or HCl. Pour 30 ml of solution into a 50-ml graduated conical centrifuge tube.

2. Add 1 ml of carrier solution containing 25 mg of ruthenium (as $RuCl_4$). Small amounts (25 mg) of hold-back carriers of Sr, Ce, Cs, Zr, or Cr may be added also, if these radionuclides are normally contained in the sample.

3. Add 2 ml of water solution containing 0.1 g/ml of either thioacetamide or thiourea.

4. Swirl the solution in the tube for thorough mixing. Place the tube in a 90 to 100°C water bath for 30 minutes.

5. Cool the solution and filter it through an "HA Millipore" filtering apparatus. Wash the brown precipitate onto the filter with a 2N HCl solution. Use tape to mount the vacuum-dried filter paper on a stainless steel disc. Count the precipitate for beta and gamma activity. (See Table I for per cent recovery by the filtration method.)

   Two alternate methods of precipitate preparation and counting were used successfully.

Planchet Method

This method involved separating and washing the precipitate by centrifuging in a 2-3N HCl solution. The precipitate was then slurried with water and plancheted with a dropper. The solid was dried under an infrared lamp and counted for beta and gamma activity. (See Table II).

Gamma-Well Counting Method

For gamma assaying, the washed precipitate was transferred with water or acid to a suitable container for gamma-well counting. (See Table III).

The other three analytical reagents were also successfully tested in the general analytical procedure. In Step 3 above, ten drops (0.5 ml) of either B-MPA, thiophenol, or BAL were added to the solution. One ml of 1% "Duponol" wetting agent was added to reduce surface tension. The above procedure was continued beginning with Step 4.

RECOVERY OF Ru^{103} AND $Ru \cdot Rh^{106}$ TRACERS

The final procedure used in this laboratory was the precipitation of ruthenium from a 3N HCl - 0.1N HF solution followed by filtration and counting.(11,12) The HF solution, found to be necessary for complete extraction of radionuclides from environmental samples, did not affect ruthenium recovery. Using thioacetamide reagent, Boni reported that the ruthenium recovery was 98.8 ±3.4%(11).

During procedural development, however, enough data were collected to show the versatility of the method. Tables I, II, and III show that ruthenium tracers were quantitatively recovered from solutions ranging from 5N HCl to 6N NaOH.

RATIO OF Ru^{103} AND $Ru\text{-}Rh^{106}$

This ratio can be determined after the separation of ruthenium isotopes from other nuclides. Each sample is counted on a gamma counter, then shielded with a 50.3 mg/cm^2 aluminum absorber and is counted on a beta counter. Low energy Ru^{103} betas are almost completely absorbed by the aluminum. The ratio of Ru^{103} to total radioruthenium is determined by comparison of beta and gamma counts with those of known standards. A similar and more detailed procedure for ratio determination was reported at Windscale.(13)

DECONTAMINATION FACTORS FOR OTHER NUCLIDES

Decontamination factors (DF's) were determined for the more common radionuclides using the thiophenol and thioacetamide ruthenium carrier sulfides. These results are shown in Table IV. Thioacetamide was later used as the precipitant for radioruthenium as described in two comprehensive fission product analysis methods.(11,12) Both methods called for an initial double precipitation of ruthenium sulfide prior to analysis of the other nuclides. The DF's for fission products and induced activities in these procedures were all greater than 10^3.

REAGENTS AND REACTION MECHANISMS

Although the ruthenium sulfides formed by the reaction of ruthenium with thioacetamide, thiourea, thiophenol, β-mercaptopropionic acid, and 2,3-dimercaptopropanal were not analyzed to determine compositions, there is evidence that both the simple and complex sulfides are formed.

Thioacetamide(14) is known to be stable in neutral solution. The reagent is readily hydrolyzed by heating with aqueous acid or alkali, thus releasing H_2S. This method of precipitation of the simple RuS_2 allows less coprecipitation of other sulfides than with the normal H_2S gas generation technique.(15)

A number of precipitates were weighed after they were dried under the infrared lamp. Precipitates formed with BAL and B-MPA weighed more than the thioacetamide precipitates within each group of samples. Since the constant limiting factor was the 25 mg of ruthenium carrier, this indicated that complex sulfides were formed with BAL and B-MPA.

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TABLE I

RECOVERY OF $Ru-Rh^{106}$ TRACER - FILTRATION METHOD

Reagent	Precipitation Solution	Per Cent Recovery Beta Count		Per Cent Recovery Gamma Count	
Thiophenol	1.5N HCl	97	100(a)	93	98(a)
BAL	1.5N HCl	89	92(a)	87	87(a)
B-MPA	1.5N HCl	95	98(a)	99	97(a)
Thioacetamide	1.5N HCl	95	95(a)	96	97(a)
BAL	5.0N HCl	94		92	
B-MPA	5.0N HCl	93		93	
Thioacetamide	5.0N HCl	95		97	
Average		95		94	

(a) Samples run in duplicate

TABLE II

RECOVERY OF $Ru-Rh^{106}$ TRACER - PLANCHET METHOD

Reagent	Precipitation Solution	Per Cent Recovery Beta Count		Per Cent Recovery Gamma Count	
Thioacetamide	0.8N HNO_3	104		97	
B-MPA	0.8N HNO_3	101		101	
BAL	0.8N HNO_3	98		94	
Thioacetamide	1.6N HNO_3	89		82	
B-MPA	1.6N HNO_3	93		94	
BAL	1.6N HNO_3	93	100(a)	93	92(a)
Thioacetamide	1.5N HCl	97	103(a)	97	100(a)
B-MPA	1.5N HCl	98	94(a)	103	98(a)
BAL	1.5N HCl	91	91(a)	97	97(a)
Average		96		96	

(a) Samples run in duplicate

TABLE III

RECOVERY OF Ru^{103} TRACER - GAMMA-WELL COUNTING METHOD

Reagent	Precipitation Solution	Per Cent Recovery
Thioacetamide	2N NaOH	73
	4N NaOH	97
	6N NaOH	91
Thiourea	6N NaOH	95
	4N NaOH	94
	2N NaOH	88
	Neutral	89
	2N HCl	109
	4N HCl	82
	6N HCl	38(a)
Average		91

(a) Not included in average

TABLE IV

DECONTAMINATION FACTORS FOR COMMON RADIONUCLIDES

Nuclide	Thiophenol, DF	Thioacetamide, DF
$Sr\text{-}Y^{90}$	> 600	> 600
$Ce\text{-}Pr^{144}$	$> 10^3$	850
$Zr\text{-}Nb^{95}$	$> 10^3$	800
Cs^{137}	450	$> 10^3$
Fe^{59}	$> 10^3$	$> 10^3$
Co^{60}	$> 10^3$	330
Cr^{51}	370	350
Zn^{65}	$> 10^3$	650
I^{131}	-	$> 10^3$