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THE DETERMINATION OF FISSION PRODUCT RUTHENIUM

by

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ABSTRACT

Improvements in Glendenin's procedure¹ for the determination of fission product ruthenium have been made. The distillation from perchloric acid has been replaced by a more rapid distillation from a dilute sulfuric acid-sodium bismuthate mixture. Conditions for the quantitative volatilization and collection of the tetroxide, as well as reduction to the dioxide, have been established. Reduction to the metal for a yield determination is no longer necessary. The analysis time has been halved and the precision has been improved by a factor of three.

INTRODUCTION

The method presently employed by most laboratories for the determination of fission product ruthenium is essentially that of Glendenin.¹ Separation from the other fission products is effected by distillation of the tetroxide in an all-glass still from fuming perchloric acid. Fission product bromine and iodine are oxidized to their halogenates prior to the distillation by sodium bismuthate and molybdenum is held back by the addition of phosphoric acid. The ruthenium is collected at 0 C in 6 N alkali and reduced to the insoluble dioxide at 100 C with ethanol. After dissolving the dioxide in hydrochloric acid, the acid solution is treated repeatedly with large excesses of magnesium metal to form a fairly reproducible metal-metal oxide which is weighed to determine a chemical yield. The metal is assayed for beta activity. The steps which follow the distillation serve only to obtain a solid sample which is suitable for both a gravimetric yield determination and a beta assay and do not propose to rid the ruthenium of other activities.

Experience in analyzing process solutions for ruthenium by this method has shown that exchange between carrier and activity does not take place until after the ruthenium has been distilled. Although the bulk of the carrier usually distills quite rapidly, the perchloric acid must be fumed for at least 15 minutes to insure the distillation of 90 per cent or more of the activity. That the addition of ruthenium carrier has little or no effect on the volatilization of ruthenium activity was borne out by a study of the precision obtained when solutions of mixed fission products were analyzed by this method. In 160 duplicate determinations by four analysts no significant improvement in precision was obtained by making a yield correction. The average deviation from the mean was 3.4 per cent; the average yield was 87 per cent.

Because the steps which follow the distillation improve neither the radioactive purity of the sample nor the accuracy of the determination, it appeared that an appreciable decrease in analysis time could be realized by eliminating these steps. In most instances dilution of the catch solution to volume and gamma counting* an aliquot of this would complete the analysis. If the ruthenium activity in the original solution was particularly low, it might be necessary to concentrate the activity in the catch solution by a quantitative reduction of the ruthenate to the insoluble dioxide.

Bismuthate-dilute sulfuric acid mixtures had been found to be particularly effective in the separation of macro amounts of ruthenium prior to its spectrophotometric determination. By using this same mixture in the fission product analysis, the speed and quantitateness of the distillation have been improved and the hazard of fuming a wide variety of samples with perchloric acid has been eliminated. Although bismuthate had been used previously with perchloric acid as a medium for the distillation of both fission product¹ and macro² ruthenium, it is now apparent that the bismuthate was rapidly reduced by water in the strongly acidic media recommended by these authors and that the only effective reagent in these distillations was perchloric acid.

In the proposed procedure the perchlorate distillation has been replaced by a distillation from 6N sulfuric acid using sodium bismuthate as the oxidant. Distillation is complete in less than 5 minutes and no special provisions for preventing the distillation of molybdenum, bromine, and iodine activities are necessary. Conditions have been established for both the quantitative collection of the tetroxide and the reduction to the dioxide so that no yield determination is necessary. The dioxide may be assayed for either beta or gamma activity; on the more active samples the sodium hydroxide catch solution may be assayed directly for gamma activity.

EXPERIMENTAL

Distillation of Ruthenium

Ruthenium is distilled rapidly as the tetroxide from a slurry of 6 N sulfuric acid and sodium bismuthate. As the temperature of the mixture nears the boiling point volatilization of the tetroxide begins and most of it distills immediately in a visible amber band. Distillation is continued for

*A gamma assay is, in general, preferable to a beta assay. The beta from ruthenium¹⁰³, the predominant isotope in most process solutions, is quite weak, 0.22 Mev, and beta assays therefore discriminate against it heavily and record primarily the 3.5 Mev beta from ruthenium-rhodium¹⁰⁶.

several minutes to insure the complete removal of ruthenium from the still. Using both exchanged ruthenium and mixtures of tracer and carrier, gamma assays of the still pots after distillation routinely showed less than 0.5 per cent of the activity remaining behind. Because reducing agents such as chloride, bromide, nitrite and oxalate may cause deposition of the ruthenium on the walls of the still, the samples are fumed with sulfuric acid prior to the distillation.

In the bismuthate-sulfuric acid distillation the concentration of the acid must be kept at or below 6 N to prevent reduction of the bismuthate by the water. In 8 N sulfuric acid the bismuthate may be completely reduced before the ruthenium is all distilled; in 12 N acid the bismuthate is reduced so rapidly that little or no ruthenium is distilled.

Collection of the Tetroxide and Reduction to the Dioxide

Since high chemical yields obtained in the perchlorate method indicated that 6 N sodium hydroxide was both reasonably efficient as a reagent for the collection of the tetroxide and satisfactory as a medium for the ethanol reduction to the dioxide, the quantitateness of each step was tested by using carrier which had been tagged with 365-day ruthenium¹⁰⁶. In the distillation step it was found that losses of up to 10 percent were occurring in the collection of the tetroxide. The use of a more concentrated sodium hydroxide catch solution, 12 N instead of 6 N, was found to be much more effective in reducing the losses of tetroxide than a proportionate increase in the volume of the 6 N hydroxide. By using 5 ml of 12 N sodium hydroxide in a 6-inch test tube the losses in the distillation step were reduced to one per cent or less.

The quantitateness of the reduction of the ruthenates and perruthenates with ethanol at 100 C was tested as a function of sodium hydroxide concentration. Above 3 N it was observed that complete reduction to a centrifugable dioxide was impossible. A green color in the supernate suggested this and a radioassay confirmed it. Below 3 N from 98 to 100 per cent of the ruthenium is reduced to a form of the dioxide which is easily filtered or centrifuged. Because the volume requirements for collecting the distillate are low, reduction of the alkali concentration from 12 N to 3 N or less by dilution can be made without increasing the volume excessively. Reduction of the alkalinity by neutralization with acid is to be avoided. The rapid disproportionation of ruthenate to tetroxide and dioxide in neutral and acid solutions could easily lead to losses by volatilization of the tetroxide.

Experience has shown that the reduction is very sensitive to impurities in the sodium hydroxide catch solution. Over a period of months the catch solution which is stored in polyethylene bottles apparently absorbs minor impurities from repeated contact with the laboratory air and/or the bottle and the reduction becomes more difficult. Carbonate was suspected

as a cause for this behavior but additions of carbonate to fresh hydroxide did not impair the reduction of ruthenium to the dioxide.

PROCEDURE

Transfer an aliquot containing from 10^3 to 10^4 ruthenium gamma or beta counts to a 50-ml beaker. Add 5 ml of 6 N sulfuric acid, 0.5 ml of ruthenium carrier (5 mg) and heat to fumes on a sand bath. (The loss of ruthenium from hydrochloric-nitric acid samples during this step is prevented by the prior addition of excess 12 N hydrochloric acid.) After cooling, carefully add 5 ml of water and stir. Transfer with several 6 N sulfuric acid washings to a still of the type shown in Figure 1. After placing the delivery arm of the still in the receiver, add 5 ml of 12 N sodium hydroxide to the receiver and a slurry of ice and water to the cooling bath. Slurry 0.5 g sodium bismuthate in 6 N sulfuric acid and transfer to the still with several 6 N acid rinses. Adjust the air supply to about 2 bubbles per second and distill until 5 ml of water has been distilled. Transfer the distillate to a 40-ml centrifuge cone with water and dilute to 25 ml. Add 5 ml of 95 per cent ethanol and heat to boiling. After the ruthenium is well coagulated, centrifuge for 10 minutes and pour off the supernate. Dissolve the ruthenium dioxide in 10 drops of 12 M hydrochloric acid, transfer to a 3-ml test tube with water and dilute to 2 ml. Assay for gamma activity in a well-type scintillation counter. If a beta assay is desired, the ruthenium dioxide is collected on a small filter paper, using a filter chimney assembly dried with alcohol, and mounted for counting.

RESULTS AND DISCUSSION

A test of the over-all ruthenium recovery in the procedure described above was made with ruthenium¹⁰⁶ tracer. In 18 analyses the recovery averaged 97 per cent and was never below 95 per cent. Radioassays of the still residues and the supernates from the alcohol reduction indicated that the ruthenium losses were primarily in the reduction step. No serious attempt has been made to improve the method further as it now meets the requirements of separations process fission product analyses.

A comparison of the accuracy of the perchlorate method to that of the new method outlined here was made on a few solutions of irradiated uranium. There was no apparent difference in the ruthenium activities as determined by the two methods. The precisions of the two methods were compared by randomly selecting 36 analysis reports of ruthenium activity in mixed fission product mixtures from the files. In 18 duplicate determinations the perchlorate method gave a standard deviation of 7.3 per cent and a maximum deviation of 20 per cent. On the same number of duplicate determinations the new method gave a standard deviation of 2.3 per cent and a maximum deviation of 7 per cent.

Figure 1.

Apparatus For The Distillation Of Ruthenium

The bismuthate-dilute sulfuric acid distillation has also been adapted to Marshall and Rickard's³ spectrophotometric determination of ruthenium. The distillation not only separates the ruthenium from interferences, but also results in a basic solution of ruthenate ions whose absorbance can be measured without further manipulation. The ruthenium tetroxide is collected at 0 C in a 25-ml volumetric flask containing 15 ml of 8 N sodium hydroxide. When the distillation is complete, the solution is warmed to 25 C, allowed to stand for 10 minutes to complete the reduction of perruthenate to ruthenate, and the absorbance measured.

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