The Separation and Determination of Ruthenium in Fission Products by Liquid-Liquid Extraction with Pyridine

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(Received January 14, 1963)

When a fission product which contains ruthenium is dissolved in nitric acid, the element goes into the solution as the nitrosylruthenium radical (RuNO) III, complexed with nitrato, nitro, hydroxo and aquo ligands[1-3]. The element may have any oxidation number between 0 and +8, according to the composition and other conditions of the solution containing its compounds. The element may exist in various ion-species, polymers and compounds in intermediate states of oxidation[4], and it has been recognized that the separation of radioactive ruthenium from an aqueous solution containing other fission products requires the use of very difficult techniques.

Various methods have been proposed for this separation by many investigators; a summary of the methods intended for practical use has been given by Wyatt and Rickard[5]. According to their description, the isolation of radioactive ruthenium is generally accomplished by electrodeposition, ion exchange, distillation, liquid-liquid extraction or reduction by light metals. All isolation procedures naturally should consist of two steps: the first, to make the oxidation number of the element in all the compounds the same, preferably the lowest or the highest (that is, to convert the element to metallic ruthenium or the tetraoxide), and the second, to separate the compounds obtained by the first step. For separating the ruthenium tetraoxide, in which the element possesses its highest oxidation number, +8, distillation is usually adopted because of the volatility of the compound from an acidic solution containing a strong oxidizing agent, such as permanganate, silver peroxide, sodium bismuthate or periodic acid[6,7]. On the other hand, separation without distillation has been attempted by liquid-liquid extraction, in which ruthenium tetraoxide in an acidic solution is transferred into carbon tetrachloride by agitating the two phases in the presence of a strong oxidant in the aqueous phase. The tetraoxide transferred into the organic phase can be stripped again into another aqueous solution containing a reducing or chelating agent, and the colored, lower oxide is estimated colorimetrically. In both distillation and liquid-liquid extraction, however, some of the ruthenium tetraoxide is easily lost during the operations because of its volatility at moderately high temperatures. It has therefore been found desirable that the tetraoxide be treated in an alkaline rather than an acidic solution. It has already been known that all ruthenium oxide can be easily oxidized by sodium hypochlorite to perruthenate in an alkaline solution[8], and that the spectrophotometric measurement of the ruthenium content of the resulting solution can be made at 385 mμ[9]. This colored solution can also be obtained by passing the gaseous tetraoxide into a solution containing 6 N sodium hydroxide and 0.05 N sodium hypochlorite. Stoner[10] and Larson and Ross[11] employed this reaction for the photometric determination of ruthenium through distillation of the tetraoxide. Although as little as 200 μg. of the element can be determined by this method, however, it cannot be employed for the minute amounts of the element that are ordinarily met with in the radiochemical separation; moreover, accurate measurement of the radioactivity of the separated nuclide is impossible on account of the self-absorption of the radiation by the large amounts of alkaline salts present in the solution.

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The present authors have found that the perruthenate ion formed in an alkaline solution, as described above, can be easily extracted by pyridine, just as the permanganate, perrhenate and pertechnetate ions can be[9,11]. The present paper describes a method for the rapid determination of radioactive ruthenium by liquid-liquid extraction.

Experimental

Radioactive Ruthenium.—Ruthenium-106 as nitrosylruthenium trinitrate in 8 M nitric acid was purchased from the Radiochemical Centre, Amersham, England, The original solution, containing 0.937 mc./ml. (assayed, 27th, Nov. 1957), was diluted with 3 M nitric acid to make its radioactivity about 1000 c. p. m. per 0.05 ml. The radiochemical purity of the ruthenium-106 was estimated to be above 99% and the radioactivity attributable to ruthenium-10^3, negligible.

Ruthenium Carrier.—Ruthenium red, that is, ruthenium oxychloride ammoniated $Ru_2(OH)_2Cl_4 \cdot 7NH_3 \cdot 3H_2O$, being regarded as a pure substance, was dissolved in water to prepare a solution containing a definite amount of ruthenium. On the other hand, 0.50084 g. of pure metallic ruthenium (Yokokawa Chem. Co., purity; over 99%) was dissolved in a small quantity of 10% "Antiformin" solution and kept for a time at 40°C. The solution was then filtered through a sintered glass G-4 into a 100 ml. measuring flask, after which the volume was adjusted to the mark with "Antiformin". This dark-brownish solution contains 5 mg. of ruthenium in one milliliter.

Chemical Reagents.—The reagents and solvents employed were all of the chemical pure grade. Among them, the solution of sodium hypochlorite was prepared from the commercial "Antiformin" with or without diluting the original solution. The "Antiformin" contains about 6 g. of active chlorine, 7.8 g. of sodium hydroxide and 32 g. of sodium carbonate per 100 ml.

Filter Paper for Chromatographic Use.—Toyo No. 53 paper (2 cm. by 40 cm.) was employed.

Spectrophotometer.—A Hitachi spectrophotometer, model EPU-2, was employed.

Measurement of Radioactivity.—A G-M counting set of the Kobe Kogyo Co., consisting of a No. 131 G-M tube (mica window; 2.8 mg./cm², counting efficiency for $^{90}Sr(^{90}Y)$: 11.7%) and a "100". scalor, was used for the β-counting, and a γ-ray spectrometer of the same company, Model-101 with a single-channel pulse height analyzer AN-105, was used for the γ-counting to identify the nuclide.

Separating Funnel.—A 30 ml. spindle-shaped separating funnel with a stout, short stem was used for the good separation of the two phases.

Shaking Machine.—The shaking of the separating funnel was effected by a vertical electric oscillator operating at 230 double strokes per minute.

The other utensils were of the ordinary laboratory type.

Experimental Results and Discussion

Paper Chromatographic Investigation.—One milliliter of a 3 N nitric acid solution of nitrosylruthenium (Ru-106) trinitrate was treated with 5 ml. of 6 M sodium hydroxide and a few drops of bromine water, and the test tube was held in a boiling water for a while till the brown color of the bromine vanished. The same quantity of the alkaline solution of radioactive ruthenium was prepared in another test tube, but instead of bromine water, 3 ml. of an "Antiformin" solution was added to it, and the mixture was left alone for a day. Paper chromatography was carried out on these two solutions and the original nitrosylruthenium (Ru-106) trinitrate solution as follows: one drop of the solution was placed on each of four strips of the chromatographic filter paper at a point 3 cm. from one end, allowed to dry in the air, and then developed chromatographically by the ascending method with four different solvents: ethanol-buthanol-NH_4CNS (50 : 50 : 50), glacial acetic acid-water (9 : 1), pyridine-water (3 : 2) and methylisopropyl ketone.

The solvent was allowed to rise about 20 cm. above the spot where the drop of the solution had been placed, and then the paper strip was dried and cut transversally into 1 cm. segments, in such a way that one of the segments included the location of the original drop. This segment was called No. 1, and the numbers from 2 to 20 were assigned to the 19 segments located higher up. Each segment was placed at the center of a counting sample pan, and its radioactivity was measured with an end-window counter. The results revealed that the pyridine-water mixture was the best for the purpose in view. Figure 1 gives the histograms obtained with this solvent.

From the figure it may be inferred that various ion species are present in the original

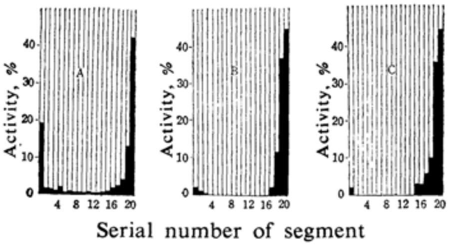

Fig. 1. Chromatograms of Ru-106 developed by pyridine-water (3 : 2).

A Original solution of nitrosylruthenium trinitrate in 3 N HNO_3

B After oxidation with bromine in sodium hydroxide solution

C After oxidation with hypochlorite in alkaline solution

solution of ruthenium nitrosyltrinitrate, but when it has been made alkaline and oxidized by bromine or chlorine, almost all the ruthenium exists in a single ion species readily distributable in pyridine. Ruthenate ions, RuO_4^{2-}, are obtained by oxidation with bromine and perruthenate ions, RuO_4^-, with hypochlorite. However, the latter may be reduced to ruthenate ions by the cellulose during the chromatographic development. The experiments with the four solvents showed that a more complete separation was effected by pyridine than by any of the others, almost all that element being carried to the solvent front, as is shown in the figure. Therefore, pyridine was adopted as the most choice solvent in the liquid-liquid extraction.

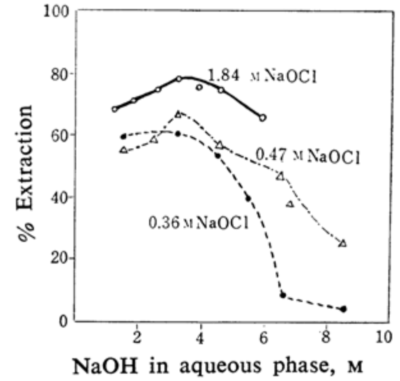

Fig. 2. Relation between % extraction of ruthenium and the concentration of sodium hydroxide and sodium hypochlorite.

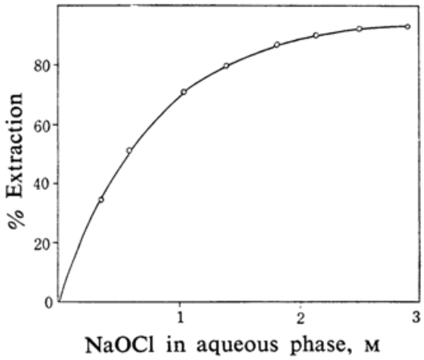

Fig. 3. Effect of concentration of sodium hypochlorite in 4 M sodium hydroxide aqueous solution.

Solvent Extraction Investigation.—To separate the perruthenate in the alkaline solution by liquid-liquid extraction, pyridine was first preferred for the above reason. In a separating funnel, 9 ml. of a sodium hydroxide solution and 1 ml. of a sodium hypochlorite solution were mixed well, and 1 ml. of a nitric acid solution of radioactive nitrosylruthenium trinitrate was added. The concentrations of sodium hydroxide and hypochlorite were so chosen as to make the final aqueous phase of predetermined concentrations. Milliliters of pyridine which had been pre-equilibrated with sodium hydroxide solutions of the corresponding working concentrations were poured into the funnel. The vessel was then tightly stoppered and shaken for five minutes with a shaking machine. After the phases had been disengaged, 1 ml. of the solution from each phase was pipetted out into a porcelain counting pan 1 inch in diameter and evaporated to dryness under an infrared lamp. The radioactivity of each sample was measured by an end-window G-M counter. The ratio of the counting rates of the two samples give the distribution coefficient of the extraction carried out under the given conditions. The dependence of the per cent extraction on the concentration of the reagents in the aqueous phase is summarily illustrated in Fig. 2. It is revealed that, at various concentrations of hypochlorite, the per cent extraction of perruthenate in pyridine is noticeably higher between three and four moles of sodium hydroxide in the aqueous phase. Next, the same experiments were carried out with varying concentrations of hypochlorite, while that of sodium hydroxide was kept constant at 4 M. The pyridine used in these experiments had been pre-equilibrated with 4 M sodium hydroxide. Figure 3 shows the increase in the per cent extraction with the increase in the concentration of hypochlorite, but even under the most favorable conditions, in which the hypochlorite increases nearly to 3 M, the per cent extraction does not exceed 92%. This seems to be due to the incomplete oxidation of ruthenium(III) to perruthenate at room temperatures, so in the next experiment the aqueous phase was kept at 100°C for two hours before the extraction, but the recovery rose only to 95.1%. It was found that when the aqueous phase was left for 24 hr. at room temperature, the recovery percentage reached 100%. Therefore, the following procedure was finally adopted. One gram of sodium hydroxide was dissolved in 10 ml. of an "Antiformin" solution and then a small volume of nitrosylruthenium trinitrate solution was added to it, after which the whole mixture was allowed to stand for a day. Thereafter, extraction was carried out with 10 ml. of pyridine pre-equilibrated with a 4 M sodium hydroxide solution.

Another problem occurred in the estimation of the radioactivity of the separated radioruthenium in the pyridine and aqueous phases. In this case the pyridine contained a small amount of sodium hydroxide, which separated

TABLE I. AMOUNTS OF SODIUM HYDROXIDE WHICH CAN REMAIN IN THE ORGANIC PHASE AFTER EQUILIBRATION

Aqueous phase	Organic phase	Maximum amount of NaOH in the organic, phase, mg./ml.
2 N NaOH 10 ml.	Pyridine 10 ml.	2.3
4 N NaOH 10 ml.	Pyridine 10 ml.	1.07
8 N NaOH 10 ml.	Pyridine 10 ml.	0.4
4 N NaOH 25 ml.	Pyridine 25 ml.	0.74
4 N NaOH 25 ml.	Pyridine 15 ml.	0.73
4 N NaOH 25 ml.	Pyridine 10 ml.	0.79
12 N NaOH 7 ml. 10% NaClO 18 ml. } 25 ml.	Pyridine 25 ml.	7.93 7.89
4 N NaOH 25 ml.	Pyridine 7 : *n*-Butyl acetate 3 } 25 ml.	0.32
4 N NaOH 25 ml.	Pyridine 1 : *n*-Butyl acetate 1 } 25 ml.	0.09
12 N NaOH 7 ml. 10% NaClO 18 ml. } 25 ml.	Pyridine 7 : *n*-Butyl acetate 3 } 25 ml.	2.85
12 N NaOH 7 ml. 10% NaClO 18 ml. } 25 ml.	Pyridine 1 : *n*-Butyl acetate 1 } 25 ml.	0.6
12 N NaOH 7 ml. 10% NaClO 18 ml. } 25 ml.	Pyridine 3 : *n*-Butyl acetate 7 } 25 ml.	0.06

out during the evaporation, mostly as sodium carbonate. The solidified salt affected the accuracy of the β-counting because of its self-absorption of the β-rays. However, it was proved that the effect was negligible if the sodium hydroxide in the sample pan did not exceed 0.2 mg./cm^2. Therefore, it was thought desirable to make the amount of sodium hydroxide in pyridine as small as possible. The amounts of sodium hydroxide present in pyridine after equilibration with aqueous solutions containing hydroxide and hypochlorite in various concentrations are shown in Table I. In order to minimize the amount of sodium hydroxide in the pyridine, it was attempted to put into it various diluents. Figure 4 shows the results obtained with *n*-butylacetate, toluene, benzene, xylene and *t*-amylalcohol as the diluent in the ratio by volume as indicated on the abscissa. The amount of ruthenium recovered was greatest when pyridine was used as the extracting solvent by itself, but a mixture of pyridine and *n*-butyl acetate was thought promising, even though only 93% of the ruthenium is recovered by it, because at a 1 : 1 volume composition it dissolved very little sodium hydroxide.

Spectrophotometric Investigation.—The absorption spectrum of the pyridine phase containing perruthenate was measured by a spectrophotometer. In this experiment a carrier ruthenium of 3.4×10^{-4} mol./l. was employed to develop the red-brownish color of the perruthenate. The wavelength-absorbancy curve of the pyridine solution, as well as the curve for pure pyridine, pre-equilibrated with 4 M

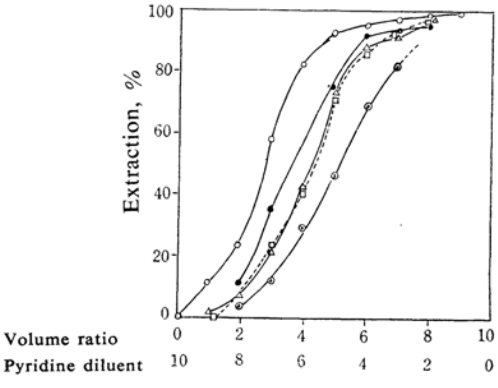

Fig. 4. Effect of diluents of pyridine on the extraction of ruthenium.

○ *n*-Butyl acetate △ Toluene
□ Benzene ● Xylene
⊙ *t*-Amylalcohol

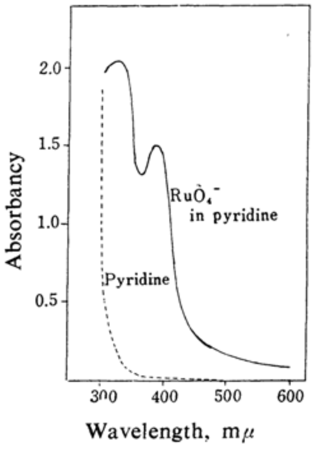

Fig. 5. Absorption spectrum of perruthenate extracted in pyridine.

sodium hydroxide is shown in Fig. 5, which agrees well with that of perruthenate in an alkaline solution obtained by Stoner⁽¹⁰⁾, by Larson and Ross⁽⁹⁾ and by Koyama⁽¹²⁾. Therefore, it may be concluded that the perruthenate extracted into pyridine has the same constitution as that in the alkaline aqueous solution.

The Separation of Radioactive Ruthenium from Fission Products.—In this study of the fission products, those nuclides were considered which would account for more than one per cent of the total radioactivity after the products had been aged for one year. The nuclides which fall in this category are zirconium-niobium-95, cerium-praseodymium-144, promethium-147, strontium-yttrium-90, cesium-137-barium-137^{m}, strontium-89 and yttrium-91. Since the chemical behavior of strontium-89 and yttrium-91 are just the same as those of strontium-90 and yttrium-90 respectively, these were excluded from the scope of the present investigation. The short-lived daughters, praseodymium-144, rhodium-106 and barium-137^{m}, are not considered in this study either.

In a separating funnel 1 ml. of a nitric acid solution of the individual radioisotope, 3 ml. of a 10 M sodium hydroxide solution and 7 ml. of "Antiformin" were well mixed, kept on a water-bath at 80°C for three hours, and then kept standing for several hours. Next, 10 ml. of pyridine, which had been pre-equilibrated with 4 M sodium hydroxide, was added, and the vessel was shaken by an electric oscillator for five minutes. Then the aqueous phase was drained into another separating funnel. From the organic phase retained in the first funnel, 1 ml. of the solution was pipetted out and its radioactivity was measured. The residual organic phase was back-washed with a washing liquid consisting of 3 ml. of 10 M sodium hydroxide and 7 ml. of "Antiformin". The washing liquid was rejected, and the organic phase was pipetted out in order to measure the radioactivity. The results obtained for each nuclide are given in Table II, which shows that the radioactive ruthenium can be extracted satisfactorily into the pyridine phase. Only cesium has a tendency to migrate into the pyridine phase, since it behaves like the sodium contained as the sodium hydroxide in the pre-equilibrated pyridine. However, it can be removed from the pyridine phase by a

TABLE II. RECOVERY AND PARTITION COEFFICIENT OF INDIVIDUAL CARRIER-FREE NUCLIDE IN SOLVENT EXTRACTION WITH PYRIDINE

Nuclide	In the first org. phase %	In the first aq. phase %	Partition coefficient
Ru-106	96.2	3.7	26.0
Cs-137	1.54	98.46	1.5×10^{-2}
Sr-90(Y-90)	0.14	99.86	1.4×10^{-3}
Pm-147	0.01	99.99	$<10^{-4}$
Ce-144	0.01	99.99	$<10^{-4}$

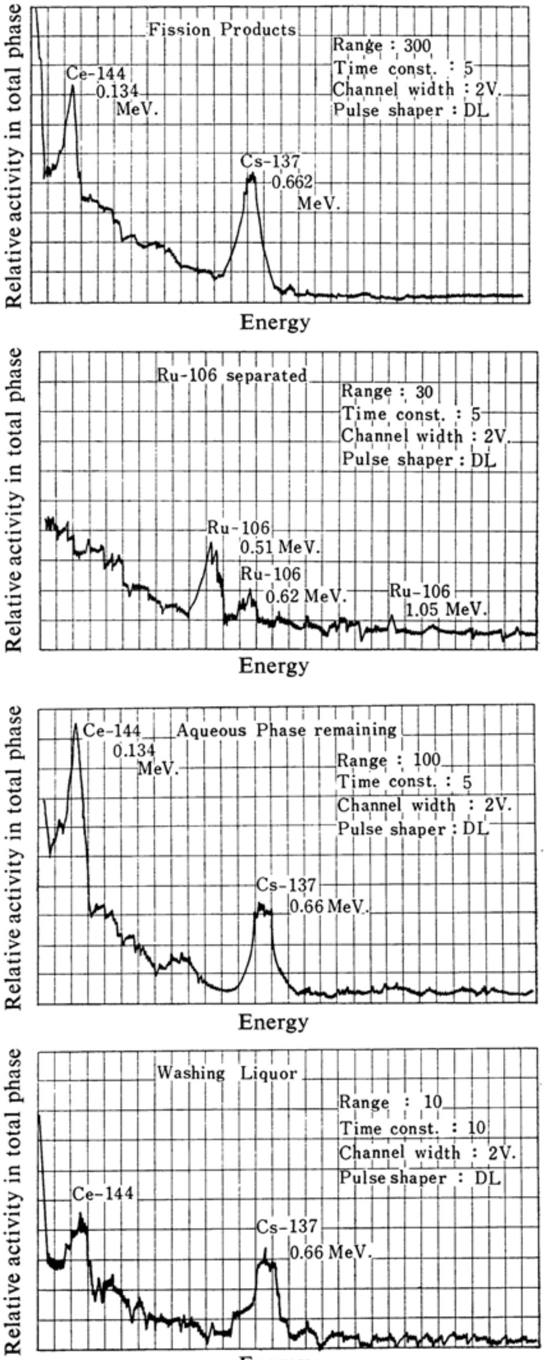

Fig. 6. Distribution of activities due to different fission products in each stage of liquid-liquid extraction.

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12) M. Koyama, *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1182 (1961).

single back-washing. The greater part of the last pyridine phase was evaporated under an infrared lamp, and its radioactivity was measured by a G-M counter. To make sure of the completion of the separation, γ-ray spectra were taken of the mixed fission products before the separation, of the residual aqueous phase, of the last organic phase after the extraction, and of the back-washing liquid, which might contain cesium-137 and cerium-144. These spectra are shown in Fig. 6. It is found that a satisfactory separation of ruthenium has been effected with little contamination by other fission products.

The Separation of Radioactive Ruthenium in the Presence of Ruthenium Carrier.—As has been described above, a perruthenate solution can also be prepared by dissolving metallic ruthenium in "Antiformin", and when this solution is treated with pyridine, the brownish-red color of the solution is completely transferred to the pyridine layer and the residual aqueous layer becomes colorless. The partition coefficient of ruthenium, by a preliminary experiment, was found to be 10^4 in the presence of 10 mg. of ruthenium between 10 ml. each of the organic and aqueous phases. Therefore, an experiment was carried out in a hope of getting a higher partition coefficient in the separation of radioactive ruthenium with a small amount of ruthenium carrier. In this experiment a definite amount of carrier ruthenium was added as perruthenate in "Antiformin" to the aqueous phase before the extraction. In the presence of 0.091 mg. to 2 mg. of ruthenium carrier per ml. of the aqueous phase, the results given in Table III were obtained; this table shows that the per cent extraction could be increased markedly by the presence of the carrier, but that the efficiency of the extraction is almost independent of the amounts of the carrier in this range. The per cent extraction was calculated as the ratio of the radioactivities of the two phases.

TABLE III. EXTRACTION OF RADIOACTIVE RUTHENIUM IN THE PRESENCE OF CARRIER

Ruthenium carrier taken in the initial aq. phase mg.	Ru-106 extracted in pyridine %	Ru-106 remaining in the aq. phase %	Partition coefficient
1.0	99.1	0.9	110
3.0	99.4	0.6	165
5.0	99.3	0.7	141
10.0	99.7	0.3	332

It was thought desirable to diminish the amount of pyridine employed so that less sodium hydroxide might accompany the dried ruthenium salt; some experiments were, therefore, carried out with smaller quantities of the solvent. The results are shown in Table IV, in which it can be seen that as much as 91.2% of the ruthenium present in 11 ml. of the aqueous phase could be extracted with as little as 2 ml. of pyridine, with the resulting presence of only 15 mg. of sodium hydroxide as an impurity.

TABLE IV. EXTRACTION OF RADIOACTIVE RUTHENIUM WITH SMALL VOLUME OF PYRIDINE IN THE PRESENCE OF 10 mg. RUTHENIUM CARRIER

Volume of pyridine used ml.	Volume of aq. phase ml.	Recovery of Ru-106 in pyridine %
11	11	99.7
6	11	96.6
4	11	95.5
3	11	91.1
2	11	91.2

The Separation of Technetium and Ruthenium by Pyridine Extraction.—Technetium can easily be extracted by pyridine[11] because it can exist in an alkaline solution as pertechnetate as its most stable form, but ruthenium can be extracted only when the perruthenate is in an alkaline solution with excess enough of a strong oxidizing agent; otherwise it is very unstable. This difference in chemical behavior between the elements was taken advantage of in effecting their separation.

Technetium-99 as potassium pertechnetate in a 0.1 M sodium hydroxide solution was taken by pipetting 0.5 ml. of the stock solution and mixing it well with 0.5 ml. of a solution of ruthenium-106 as nitrosylruthenium trinitrate in 3 M nitric acid in a separating funnel; then 4 ml. of 12 M sodium hydroxide was added, the total volume thus becoming 5 ml. To this solution was added 5 ml. of pyridine preequilibrated with 4 M sodium hydroxide. The funnel was shaken well for five minutes, and after the two layers had been disengaged, the lower aqueous layer was drained out through the stem into another funnel. One milliliter of the organic phase was pipetted into a counting pan and evaporated to dryness, and its radioactivity was measured by a G-M counter. Here the observed value was corrected for the self-absorption of the radioactivity by the sample. This count must be due to the technetium-99 separated by pyridine, for a Harley plot of the sample with a reference of calcium-45 agreed well with that of a pure technetium-99 within the range of permissible errors, showing its radiochemical purity to be above 99.5%. To the aqueous phase in the second separating funnel, 10 ml. of "Antiformin" and 5 ml. of pyridine were added, and the funnel was shaken well for five minutes. In this case there was 15 ml. of the aqueous phase and only 5 ml. of the organic phase. After separating the two phases, 1 ml. of the organic layer was pipetted and its radioactivity was measured as above. This radioactivity is presumed to be due to ruthenium-106 separated into pyridine as perruthenate. As the per cent extraction of technetium in the first step could not reach 100%, but only about 94%, some residual technetium might be present in this sample. However, the energy of the β-ray of technetium-99 is so weak that it can be eliminated by an aluminum absorber of about 40 mg./cm^2, while the β-ray of ruthenium-106 has higher energy and is scarcely absorbed by the same absorber. Technetium and ruthenium can be almost completely separated by this procedure.

Summary

The present paper has described a method of separating, by liquid-liquid extraction with pyridine, radioactive ruthenium from fission products and technetium in an aqueous solution containing sodium hydroxide and hypochlorite. In the process, ruthenium in various ionic forms and various oxidation states is oxidized to perruthenate with the hypochlorite, and the perruthenate is transferred into pyridine from the aqueous solution. The partition coefficient of perruthenate was estimated for the carrier-free and the carrier-containing cases, as well as for the case where other fission products were present. Good separation of radioactive ruthenium from other fission products was achieved by this method, with a large decontamination factor. The results were examined by a γ-ray spectrum measured at each step of the extraction process.

The authors wish to express their thanks to Dr. Shigeru Ohashi and Dr. Kikuo Terada for their advice and criticism. A part of the expenses for this study was defrayed by a grant from the Ministry of Education, to which the authors' thanks are due.

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