Separation of Fission Products by Liquid-Liquid Extraction with Cupferron-Chloroform

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Workers in various fields of study are looking for methods of rapidly separating radioactive strontium and cesium from solutions containing fission products. Before such separation is attempted, preliminary elimination of other nuclides and non-radioactive ions must be accomplished. When the precipitation method is employed for this purpose, some carrier must be added to the solution and some loss of the radioactive elements in question results from adsorption by the precipitate. Also the method takes a considerable length of time.

The solvent extraction method can be carried out rapidly and simply without any carrier. The aim of the investigation described in this paper was to establish a new method of liquid-liquid extraction by which the radioactive strontium and cesium are retained in the aqueous solution, while other metallic ions are transferred into the organic phase. The strontium and cesium may be further separated conveniently by the TTA-hexone extraction method as described in another paper by the present authors. The extracting agent for this purpose should be a compound which easily combines with various metallic ions, and forms chelated compounds, readily soluble in some organic solvent. Cupferron was chosen for the purpose for this reason.

Cupferron (nitrosophenyl hydroxylamine) is easily obtainable as an ammonium salt, which is a common reagent; it forms chelated compounds with zirconium in strong acids[1], with ter- to quinqui-valent metallic ions in weakly acidified solutions[2], and with rare earths in solutions whose pH is between 3 to 4[3], and produces precipitate when large amounts of these ions are present. Both the reagent and the chelated compounds are soluble in chloroform, with which they are easily removed from the aqueous solution. These characteristics of the

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[1] N. H. Furman, W. B. Marson and J. S. Pekola, *Anal. Chem.*, **21**, 1355 (1949).

[2] D. Dyrssen and V. Dahlberg, *Acta Chim. Scand.*, **7**, 1186 (1953).

[3] A. I. Popov and W. W. Wendlandt, *Anal. Chem.*, **26**, 883 (1954).

reagent were found very useful in the treatment of an aqueous solution containing fission products.

Experimental

Reagent and apparatus.—*Cupferron Solution, 5%.*—The reagent of extra pure grade was dissolved in water immediately before use.

Gross Fission Products.—A drop of nitric acid solution of gross fission products, imported from Oak Ridge National Laboratory, U. S. A. (Batch No. 35; cooling period, about three years) was diluted with 0.02 N hydrochloric acid so that 0.2 ml. of the solution possessed an activity of 10,000 cpm.

Other Radioisotopes.—^{90}Sr(^{90}Y), ^{95}Zr(^{95}Nb), ^{137}Cs, ^{106}Ru(^{106}Rh), ^{144}Ce, and ^{147}Pm were used and their behavior during the solvent extraction with cupferron was examined.

Buffer Solution.—0.5 M solution consisting of acetic acid, ammonium acetate, and aqueous ammonia was used, and the pH was measured by a glass electrode pH-meter.

Activity Measurement.—For β-radiation, a counting set made by the Kobe Kogyo Co. Ltd., Japan (No. 131 G-M tube: mica window, 2.2 mg./cm^2, counting efficiency: 11.7% for ^{90}Sr(^{90}Y)) was employed; for γ-radiation, a counting set made by Nuclear Instrumental and Chemical Corp., U. S. A., (sodium iodide scintillation tube, and Model D 47 counting equipment with lead absorber) was used.

Separatory Funnel.—A 30 ml. and a 300 ml. spindle shaped separatory funnel having a big short stem were used for good separation of the two phases.

Shaking Machine.—Shaking was effected by a vertical electric oscillator with 230 double strokes per minute. Up to six separatory funnels can be loaded on the shaker at a time.

Other chemicals used were all of extra pure grade and the utensils were of the ordinary laboratory type.

Procedure.—1) In a 30 ml. separatory funnel place 0.2 ml. of a solution of the gross fission products or radioisotopes, and 5 ml. of 1 to 7 N hydrochloric acid or 5 ml. of the buffer solution, and make up the volume with water to 6 ml. Then, add 1 ml. of the cupferron solution and 2 ml. of chloroform, successively. Shake the contents of the vessel for five minutes. After the phases have disengaged, transfer the organic phase into another funnel and add to it 5 ml. of hydrochloric acid or the buffer solution, and shake with the organic phase for five minutes. To the aqueous phase retained in the first funnel add again 1 ml. of the cupferron solution and 2 ml. of chloroform, and shake for five minutes. Combine the aqueous phases from the first and the second funnel in a centrifuge tube, and the organic phases in another tube and centrifuge them for about two minutes to separate the phases completely from each other. Transfer each phase to a porcelain counting dish and evaporate to dryness under an infrared lamp, and then measure the radioactivity by the counting set. Draw off the decay and the Harley plot of the activity, if necessary, to identify the nuclide isolated.

2) When various metallic ions other than fission products are present, the following procedure was adopted, by which the radioactive strontium and cesium were retained in the solution unaccompanied by other metallic ions.

Put 100 ml. of a solution containing 10 mg. of iron(III), thorium(IV), and uranyl(II) ions and fission products in a 350 ml. separatory funnel, and adjust its acidity to 1 N hydrochloric acid. Add 2 ml. of the cupferron solution and 5 ml. of chloroform, and shake for five minutes. Take out the organic phase from the first funnel and retain the aqueous phase in the vessel. Repeat the same extraction process in the first funnel till further addition of the cupferron solution produces no precipitate and the aqueous phase becomes colorless. The organic phase separated after each extraction should be collected in another funnel and washed with an equal volume of 1 N hydrochloric acid. The washing should be added to the solution in the first funnel. By this process, iron(III) is completely removed from the solution.

After the removal of iron(III), add 3 N hydrochloric acid to restore to 1 N hydrochloric acid the acidity of the solution, which has been lowered by the successive entrainments of the cupferron solution. Add 2 ml. of the cupferron solution and 10 ml. of ethyl acetate, and shake for two or three minutes. Drain the aqueous phase from the first funnel into the second, and repeat the extraction with cupferron and ethyl acetate. Collect the ethyl acetate phase retained in each extraction in the first funnel and wash the contents with an equal volume of hydrochloric acid. Add the washings to the solution in the third funnel. Thorium(IV) is transfered to the ethyl acetate phase by this extraction.

Add 20 ml. of 3% zinc amalgam to the solution in the second or the third separatory funnel, stopper well, and shake vigorously for five minutes to reduce the uranyl ion which does not combine with cupferron to uranium(IV). After removing the amalgam through the stem, add 2 N aqueous ammonia drop by drop till the pH of the solution becomes 1.8. Then add 2 ml. of the cupferron solution and 10 ml. chloroform, and shake the content for five minutes. Repeat the extraction till further addition of cupferron produces no precipitate. By this treatment the uranium is completely removed, going into the organic phase that is discarded after the extraction.

Add 2 N aqueous ammonia to the solution retained in the separatory funnel to adjust the pH to 4. Add again 2 ml. of the cupferron solution and 10 ml. chloroform, and shake for five minutes. By the last extraction rare earths of the fission products and non-radioactive metals are transferred into the chloroform phase. If necessary, repeat the extraction.

The separated aqueous phase which contains the radioactive strontium and cesium and possibly some unextractable cations, may be given additional treatments of separation, for example, with TTA-hexone.

3) The behavior of the various radioisotopes were examined throughout all the stages of the extraction described above, and the percentages of the nuclides recovered were noted.

Results and Discussion

After the extraction was carried out by Procedure 1 on the aqueous solution of the gross fission products at different pH, the separated organic phase was evaporated to dryness and the radioactivity was measured by means of a G–M β-counting set. The ratio of the counting rate (cpm.) of the organic phase to that of the original solution represents the amount extracted of the gross fission products. As illustrated in Fig. 1, the ratio reaches its maximum of 81% at pH 4 and decreases slightly as the pH of the solution increases still further, probably because of formation of radiocolloid in the solution. Evaporation of the chloroform containing cupferron may be readily accomplished with an infrared lamp, and the residue transformed into the oxide by ignition to red heat. Therefore, the stripping of the nuclide from the organic phase was not found necessary.

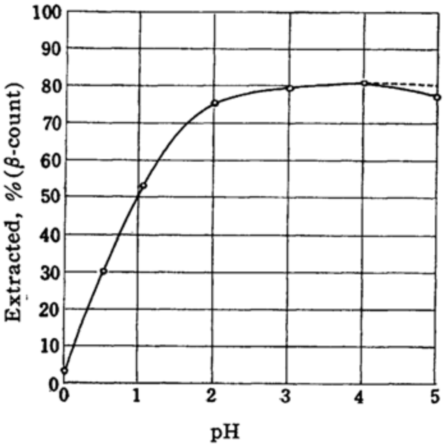

Fig. 1. Effect of pH on the extractability of gross fission products by cupferron-chloroform.

To find what nuclides could be extracted from the mixed gross fission products into the organic phase, the extraction was done with the solution containing ^{106}Ru, ^{137}Cs, ^{90}Sr(^{90}Y), and rare earths that had been separated as a fraction of the fission products by the cation exchange resin method[4]. The results of the experiments for each nuclide is shown in Fig. 2., from which it is found that rare earths and yttrium go into the organic phase at pH 4, and cesium, strontium and ruthenium remain in the solution.

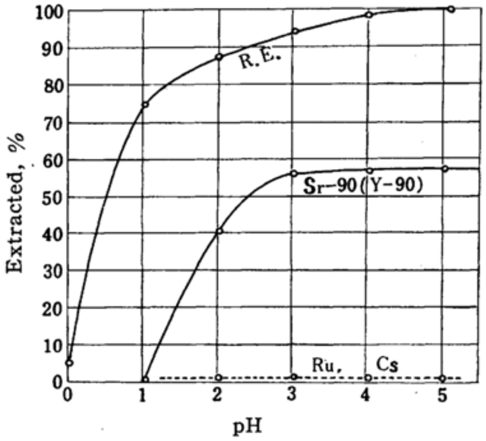

Fig. 2. Effect of pH on the extractability of some nuclides in fission products by cupferron-chloroform.

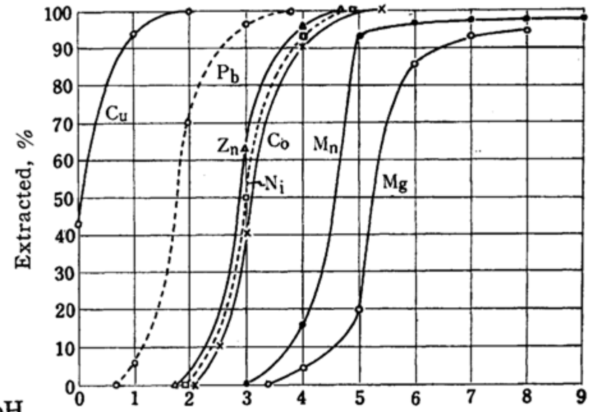

Fig. 3. Effect of pH on the extractability of various metallic ions by cupferron-chloroform.

The extraction of other non-radioactive metallic ions at different pH is shown in Fig. 3. Many ions can be removed into the cupferron-chloroform while the acidity of the solution is higher than pH 4.

One hundred ml. of the solution containing the gross fission products together with iron(III), thorium(IV), and uranyl(II) ions, was treated by successive extractions of Procedure 2. The aqueous phase

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[4] M. Honda, Y. Sasaki and H. Natsume, *Japan Analyst* (*Bunseki Kagaku*), **4**, 240 (1955).

TABLE I

EXTRACTION OF FISSION PRODUCTS AND RADIOISOTOPES BY CUPFERRON-CHLOROFORM

Amounts taken or original radioactivity	Percentage of radioactivity in the last aqueous phase %
Fe(III) : 10 mg. Fission products : 10,000 cpm.	18.05(^{90}Sr and ^{137}Cs)
Fe(III) : 10 mg. ^{137}Cs : 10,000 cpm.	100. (^{137}Cs)
Fe(III) : 10 mg. ^{90}Sr(^{90}Y) : 10,000 cpm.	42.5 (^{90}Sr)
Fe(III) : 10 mg. U(VI) : 5 mg. Th(IV) : 10 mg. Fission products : 10,000 cpm.	20.3 (^{90}Sr, ^{137}Cs and ^{106}Ru) 15.9 (after the Ru was expeled by distillation)

TABLE II

RESULTS OF TWO-STEP EXTRACTION WITH CUPFERRON-CHLOROFORM AND TTA-HEXONE

Material taken or original radioactivity in original solution	Percentage of radioactivity extracted in TTA-hexone phase %	Percentage of radioactivity retained in the last aq. phase %
Fe(III) : 10 mg. ^{137}Cs : ca. 10,000 cpm.	0.	100.
Fe(III) : 10 mg. ^{90}Sr(^{90}Y) : 10,000 cpm.	42.1 (^{90}Sr)	0.36 (^{90}Sr)
Fe(III) : 10 mg. ^{106}Ru : ca. 10,000 cpm.	1.5 (^{106}Ru)	97.9 (^{106}Ru)

remaining at the end was evaporated and the radioactivity was measured to determine the recovery of the radioactive substances. Very satisfactory results were obtained in each case as shown in Table I.

The aqueous phase remaining after the solvent extraction with cupferron-chloroform was next subjected to treatment with TTA-hexone as described in the following paper, and strontium was extracted into the organic phase. The two-step extraction gave the results shown in Table II, and the strontium in the original solution could be separated rapidly and quantitatively from the gross fission products.

Summary

In order to separate rapidly the radioactive strontium and cesium from the solution containing gross fission products and other non-radioactive metallic ions, cupferron-chloroform extraction was attempted. By changing the acidity of the aqueous solution from 1 N hydrochloric acid to pH 4, and by performing extractions in each stage, the strontium and the cesium could remain in the aqueous phase, while the other could be removed into the organic phase. The radioactive strontium may be extracted in the organic phase by the following extraction with TTA-hexone at pH 8.

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