The Solvent Extraction of Ruthenium with 8-Hydroxyquinoline

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Because of the difficulty of separating it, ruthenium has prompted studies of a simple and effective method for separation; various isolation schemes for radioactive ruthenium from a fission product mixture have already been reported.[1-5]

The solvent extraction of radioruthenium was accomplished; ruthenium was transferred as its tetroxide into carbon tetrachloride,[4] as perruthenate into pyridine[5] or as its thiocyanate complex into various organic solvents.[6]

On the other hand, numerous organic reagents which can react with ruthenium have been employed for the colorimetric determination, but heating is generally required to develop the color.[7-15]

It has also been stated that in an acetate medium 8-hydroxyquinoline forms a green complex with ruthenium(III) which is extractable

1) C. D. Coryell and N. Sugarman, "Radiochemical Studies," "The Fission Products 2," New York (1951), p. 3.
2) D. N. Hume, ibid., "3" New York (1951), p. 1557.
3) D. L. Love and A. E. Greendale, *Anal. Chem.*, **32**, 780 (1960).
4) J. W. T. Meadows and G. M. Matlack, ibid., **34** 89 (1962).
5) T. Kiba, A. Miura and Y. Sugioka, This Bulletin, **36**, 663 (1963).
6) Y. Oka and T. Kato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 249 (1963).
7) G. H. Ayres and F. Young, *Anal. Chem.*, **22**, 1277 (1950); **22**, 1281 (1950).
8) R. P. Yaffe and A. F. Voigt, *J. Am. Chem. Soc.*, **74**, 1503 (1952); **74**, 5043 (1952); **74**, 3163 (1952).
9) A. Musil and R. Pietsch, *Z. anal. Chem.*, **137**, 259 (1952).
10) J. E. Currah, A. Fischel, W. A. E. McBryde and F. E. Beamish, *Anal. Chem.*, **24**, 1980 (1952).
11) W. Geilman and R. Neeb, *Z. anal. Chem.*, **152**, 96 (1956).
12) S. B. Knight, R. L. Parks, S. C. Leidt and K. L. Parks, *Anal. Chem.*, **29**, 571 (1957).
13) C. V. Banks and J. W. O'Laughlin, ibid., **29**, 1412 (1957).
14) D. L. Manning and O. Menis, ibid., **34**, 94 (1962).
15) Y. Oka and T. Kato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 254 (1963).

with chloroform,[16] but the experimental conditions of the complex formation, as well as its extraction behavior, are not known in detail.

In the present work, the investigation of the solvent extraction hehavior of ruthenium with 8-hydroxyquinoline was carried out using radioactive ruthenium, ruthenium-106, as a tracer.

Extraction can also be applied for the removal of the tracer amounts of ruthenium that are ordinarilly met with in the radiochemical separation.

Experimental

Ruthenium Stock Solutions.—A hydrochloric acid solution of ruthenium(IV) was prepared by dissolving "ruthenium trichloride" obtained from the Yokosawa Chem. Co. in 6 M hydrochloric acid.[17] The ruthenium content of this solution was determined as 1.93 mg. Ru/ml. by the method of Taimni.[18]

A nitric acid solution of ruthenium(IV) of a known ruthenium content (1.6 mg. Ru/ml.) was prepared by absorbing gaseous ruthenium tetroxide into 1 N nitric acid containing 3% hydrogen peroxide followed by heating it at 40°C for 30 min. The ruthenium tetroxide was prepared according to Kambara's method,[19] in which "ruthenium trichloride" was oxidized with lead peroxide in a sulfuric acid medium.

A more dilute solution containing 10 μg. Ru/0.1 ml. was prepared by diluting the stock solutions just before use; in every extraction experiment, a 0.1 ml. aliquot of this solution was used.

Radioactive Ruthenium. — Ruthenium-106 as "trichloride" in 8 M hydrochloric acid, with a radiochemical purity of about 99%, was imported from the Radiochemical Centre, Amersham, England. A part of this was diluted with 0.1 M hydrochloric acid to make its radioactivity about 5×10^4 c. p. m./0.1 ml.; this was used as a tracer of ruthenium(IV) in hydrochloric acid. Another part of this was converted into a nitrate solution in the same manner as was described for inactive ruthenium nitrate. This was used as a tracer of the corresponding ruthenium(IV) nitrate after proper dilution with 0.1 M nitric acid, also with a radioactivity of about 5×10^4 c. p. m./0.1 ml.

8-Hydroxyquinoline and Other Chemical Reagnts. — Commercial 8-hydroxyquinoline of guaranteed grade, with the observed melting point of 72.5~74.5°C, was used.

The organic solvents and other reagents were all guaranteed grade reagents. Redistilled water was used.

Apparatus.—For the measurement of the radioactivity, a well-type scintillation counter, Model RSP-1, made by the Kôbe Kôgyô Co., Japan, was employed. For measuring the pH of the aqueous phase, a glass electrode pH meter, Model EHM-1, made by the Hitachi Co., Japan, was employed.

Experimental Procedure.—The procedure for the extraction experiment was, unless otherwise stated, as follows: To an aliquot of 8-hydroxyquinoline dissolved in *n*-propanol or in 10 M acetic acid in a test tube, an aqueous buffer and, if needed, another reagent solution were added to adjust the pH value of the solution, and the total volume was made up to 6 ml. with water. A 0.1 ml. portion of each ruthenium-106 and ruthenium solution (Ru : 10 μg.) was added, and the mixture was kept at an elevated temperature (60°C in most cases) in a constant temperature bath for a time.

After having been cooled in running water, the contents were transferred into a separatory funnel, and the 8-hydroxyquinolate formed was extracted with a suitable aliquot of an organic solvent (2 or 5 ml.) like *n*-butanol or benzene by shaking it for 1 min. An excess quantity of 8-hydroxyquinoline was employed in every extraction system; viz., 2 ml. of 0.05 M 8-hydroxyquinoline (100 μeq.) in *n*-propanol or 1 ml. of 1 M 8-hydroxyquinoline (1 meq.) in a 10 M acetic acid solution was used.

In all extractions, both the organic and aqueous phases, after having been disengaged in a separatory funnel, were drained into two test tubes. The respective ruthenium contents were then estimated by gamma counting, and the percentage extraction was computed as a ratio of the counting rate of the organic extract to the sum of the counting rates of the two phases. The pH of the aqueous phase after extraction was also measured.

Results and Discussion

The Formation of 8-Hydroxyquinolate. — In the preliminary study of the extraction of ruthenium as 8-hydroxyquinolate, it was found that the rate of the formation of 8-hydroxyquinolate, as well as of the extraction, was quite slow at room temperature when an aqueous solution containing ruthenium was shaken with 8-hydroxyquinoline in chloroform, even at relatively high pH values (pH 4~6) and at a high concentration of the reagent (1 M). The formation of the 8-hydroxyquinolate, however, was accelerated when an aqueous solution was kept at an elevated temperature in the presence of an excess reagent as its *n*-propanol solution, so the following equilibrium extraction might be achieved rapidly by shaking it with an additional organic solvent such as chloroform.

As is shown in Fig. 1, the extraction of 8-hydroxyquinolate with 2 ml. of chloroform or *n*-butanol from an aqueous phase under various conditions was accomplished after the aqueous system had been kept at 60°C for 1 hr.

Ruthenium(IV) nitrate was used in this experiment; it will also be used hereafter unless otherwise indicated.

16) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publisher, New York (1959), p. 791.

17) The predominant species in this solution was $Ru(OH)_2Cl_4^{2-}$, as will be described in a later part of this paper.

18) I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, **11**, 329 (1954).

19) T. Kambara, *Japan Analyst*, **7**, 439 (1958).

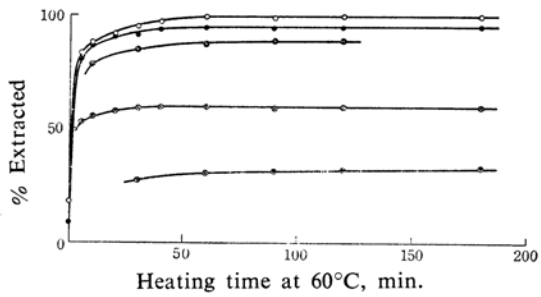

Fig. 1. Effect of heating time on the extraction.
○ pH 6.0 (HOAc - 0.33 M NaOAc), *n*-Butanol
● pH 6.0 (HOAc - 0.33 M NaOAc), Chloroform
◎ pH 3.9 (HOAc - 0.33 M NaOAc), Chloroform
⊗ pH 8.5 (NH_4OH - 0.33 M NH_4Cl), Chloroform
⊙ pH 1.2 (HNO_3 - 0.33 M NaOAc), Chloroform

Extraction Solvent. — The ruthenium 8-hydroxyquinolate formed in an aqueous acetate medium of pH 6 in the manner described above was extracted with each 2 ml. portion of various organic solvents. As is shown in Table I, more than 99% of the original ruthenium is transferred into various organic solvents, except isopropyl ether. *n*-Butanol is especially efficient in retaining 8-hydroxyquinolate.

TABLE I. EXTRACTION BY VARIOUS SOLVENTS

Solvent	% Extracted
n-Butanol	99.3
Isoamyl alcohol	96.4
Cyclohexanone	97.0
Methyl isobutyl ketone	94.5
Isopropyl ether	84.0
Isoamyl acetate	92.1
Benzen	93.0
Carbon tetrachloride	90.1
Chloroform	94.8

Extraction Curves. — The determination of the pH range where the extraction of ruthenium has to be successful was carried out.

The shape of the extraction curve is generally affected by the buffer component employed to adjust the pH of an aqueous phase, thereby emphasizing the importance of the proper selection of the buffer component and its concentration in a system.[20-22]

First, extraction with 2 ml. of *n*-butanol from an aqueous acetate system composed of 0.33 M sodium acetate or ammonium acetate was carried out, varying the pH values with additional dilute nitric acid, acetic acid, or aqueous ammonia. The extraction curve thus obtained is illustrated in Fig. 2, from which the extraction of ruthenium of either tracer (ruthenium-106, carrier-free) or ordinary micro amounts (Ru : 10 μg.) may be found to be almost complete by using 2 ml. of *n*-butanol at the pH value of 4~6.

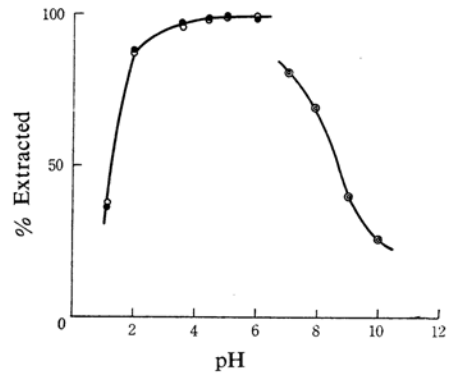

Fig. 2. Effect of pH on the extraction from acetate buffers.
● Ru : carrier-free
○, ◎ Ru : 10 μg.

In an aqueous ammonia - ammonium acetate system, extractability is reduced by an interfering action of the ammonium ion, as will be described later on. Hence, the discontinuity of the extraction curve appeared at about pH 6.

Next, the relation between the percentage extraction of ruthenium and the pH of the aqueous solution containing various buffer components, viz., 0.03 M phthalate, 0.1 M citrate, 0.03 M or 0.1 M phosphate, or an aqueous ammonia - ammonium chloride mixture was investigated. An aqueous solution of sodium hydroxide was used to give the aqueous solution higher pH values. Extraction was also carried out with 2 ml. of *n*-butanol.

The results are illustrated in Fig. 3. In the phthalate system, as well as in the case of acetate, an almost complete extraction was achieved at the pH range of 4~6, but in this pH region extraction is considerably reduced in the presence of citrate. Phosphate and ammonium salts were also unfavorable as buffer components.

Coexisting Substances. — The effects of the coexistence of inorganic salts and organic acids or their salts are given in Table II. With large amouts of chloride, nitrate, sulfate and borate, no significant interferences were observed, but with oxalate and other organic substances, severe interferences resulted.

The Amount of Ruthenium.—The concentration dependence of ruthenium on the extractability was determined in an extremely low

20) H. Irving, C. F. Bell and R. J. P. Williams, *J. Chem. Soc.*, 1952, 356.
21) N. Suzuki, *Japan Analyst*, 8, 283 (1959).
22) F. P. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, 57, 294 (1953).

TABLE II. EFFECTS OF COEXISTING SUBSTANCES

Coexisting substance	Added as	Concn., M	% Extracted*	pH
Chloride	NaCl	0.4	99.2	5.2
Nitrate	$NaNO_3$	1.3	99.2	5.1
Sulfate	Na_2SO_4	0.2	98.9	5.4
Ammonium salt	NH_4Cl	0.3	91.7	5.3
Borate	H_3BO_3	0.02	97.2	5.5
Phosphate	KH_2PO_4	0.05	81.5	5.7
Citrate	$Na_2HC_6H_5O_7$	0.05	71.1	5.6
Tartrate	$Na_2C_4H_4O_6$	0.05	83.1	5.6
Oxalate	$H_2C_2O_4$	0.05	25.4	5.4
EDTA	EDTA-2Na	0.01	27.3	5.5
Hydroxylamine	$NH_2OH \cdot HCl$	0.02	31.0	5.5
None	—	—	99.3	5.6

* With 2 ml. of *n*-butanol.

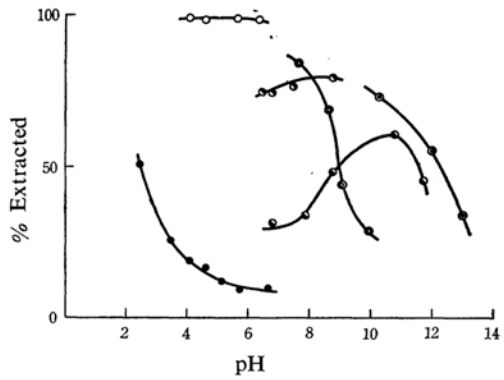

Fig. 3. Effect of pH on the extraction from phthalate, citrate, phosphate and ammonium buffers.
- ○ 0.03 M phthalate
- ● 0.1 M citrate
- ◔ 0.03 M phosphate
- ◕ 0.1 M phosphate
- ◎ 0.3 M ammonium chloride - ammonia
- ⊙ aqueous sodium hydroxide

concentration, from a tracer amount to 2.5×10^{-3} M, in an original aqueous solution. In this experiment, a definite amount of ruthenium(IV) was added to an aqueous solution containing a carrier-free ruthenium-106 tracer, and extraction with 2 ml. of *n*-butanol was carried out at pH 5.6 after heating the solution with an excess reagent, as has been described above.

As is shown in Table III, as much as 99% of the original ruthenium(IV) could be transferred into *n*-butanol as its 8-hydroxyquinolate.

TABLE III. EFFECT OF AMOUNT OF RUTHENIUM

Amount of Ru added, mg.	% Extracted
Carrier-free	99.3
0.01	99.3
0.15	99.1
1.5	99.5

The Extraction of Ruthenium Added as "Trichloride." — As the course of the extraction seemed to consist of the formation of 8-hydroxyquinolate in aqueous - *n*-propanol - acetate systems and its distribution into the organic solvent, the effect of the heating time, the concentration dependence of ruthenium and the pH range for complete extraction were also investigated when both of ruthenium and ruthenium-106 solutions were added as "trichloride" in hydrochloric acid. The results presented in Figs. 4, 5 and 6 show that the percentage extraction reaches a limiting value upon one hour's heating at 60°C and that the value is held constant over a wide concentration range of ruthenium; almost complete extraction can be achieved in the pH range of 4~6 by 2 ml. of *n*-butanol. This behavior is closely similar to that observed in the case of nitrate, in which the oxidation state of ruthenium is quadrivalent.[23] As is shown in Table II. extraction was, however, reduced to an appreciable extent in the presence

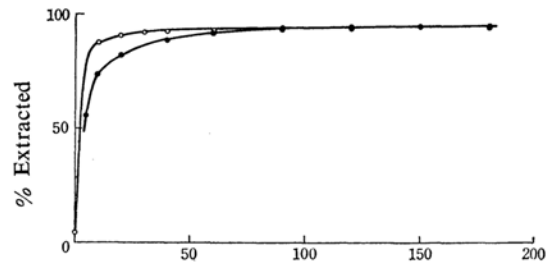

Fig 4. Effect of heating time on the extraction (Ruthenium was added as "trichloride").
- ○ pH 5.6, Chloroform
- ● pH 4.4, Chldroform

23) J. S. Anderson and J. D. M. McConnell, *J. Inorg. Nucl. Chem.*, 1, 371 (1955).

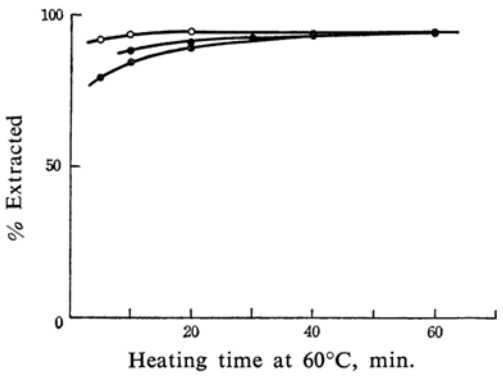

Fig. 5. Effect of heating time on the extraction in different amount of ruthenium (added as "trichloride").
pH 5.6 acetate buffer, chloroform
⊗ Ru: carrier-free
● Ru: 10 μg.
○ Ru: 100 μg.

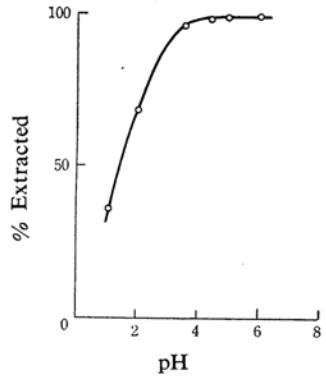

Fig. 6. Effect of pH on the extraction from acetate buffers (Ruthenium was added as "trichloride").
Solvent: 2 ml. of *n*-Butanol

of hydroxylamine hydrochloride, which reduces ruthenium(IV) to tervalent.[24] It has been mentioned that ruthenium(III) in hydrochloric acid is fairly air-oxidized to the ruthenium(IV) state; hence, a commercial water-soluble ruthenium trichloride is usually composed, at least in part, of ruthenium(III) salt.[25]

Indeed, when "ruthenium trichloride" was dissolved in 6 M hydrochloric acid, its absorption spectrum was characterized by intense peaks at 385 and 254 mμ, together with a minor peak at 476 mμ corresponding to that of the chloro-ruthenium(IV) species; according to Wehner's paper,[26] this was defined as $Ru(OH)_2Cl_4^{2-}$. Air-oxidation occurred to both inactive and radioactive ruthenium; therefore, the extraction behavior of 8-hydroxyquinolate has to be identical with that of ruthenium(IV).

The Improvement of the Extraction System. — Thus the extraction of ruthenium in *n*-butanol as 8-hydroxyquinolate is completed from an aqueous *n*-propanolic solution, but the back extraction of ruthenium from an organic extract composed of a *n*-propanol - *n*-butanol mixture can not be performed because of the water-miscible property of this solvent mixture. Therefore, it is desirable to modify an extraction system so as to produce a favorable separation of ruthenium from the organic extactants. On the other hand, it is also desirable to make the rate of approach to the extraction equilibrium higher than has been observed in previous parts. Consequently, the behavior was further examined in a system involving the formation of 8-hydroxyquinolate with a still larger amount of the reagent and subsequent extraction with an almost water-immiscible solvent such as benzene.

Hereafter, ruthenium(IV) nitrate was again used, and the aqueous phase was prepared by adding an acetic acid solution of 8-hydroxyquinoline (up to 1 meq.) and adjusting the pH of the resulting solution to 4 with an additional 1 ml. portion of 2 M sodium acetate, as has been described in the Experimental section.

The effect of heating time on the extractability is shown in Fig. 7, where the percentage extraction in an equilibrium extraction with 2 ml. of *n*-butanol reaches a constant value of 99.3% with 1 meq. of the reagent after being heated for 30 min. at 60°C or for 10 min. at 80°C. In these cases, 99.0% of the ruthenium

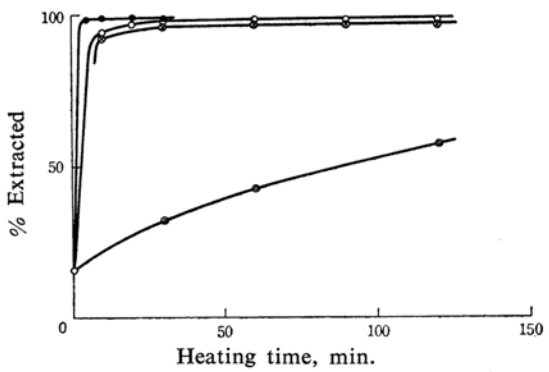

Fig. 7. Factors affecting the rate of approach to extraction equilibrium.
● 80°C, 8-Hydroxyquinoline: 1 meq.
○ 60°C, 8-Hydroxyquinoline: 1 meq.
⊗ 60°C, 8-Hydroxyquinoline: 0.1 meq.
◎ 20°C, 8-Hydroxyquinoline: 1 meq.

24) F. P. Treadwell and W. T. Hall, "Analytical Chemistry I," John Wiley & Sons., New York (1930), p. 563.
25) G. Brauer, "Hanbduch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1953), p. 1195.
26) P. Wehner and J. C. Hindman, *J. Phys. Chem.*, **56**, 10 (1952).

is extracted with 5 ml. of benzene. It may also be seen that the formation of 8-hydroxyquinolate at room temperature is unfavorably slow. The percentage extraction reached 78% after the aqueous phase had stood for about 40 hr. In the presence of 100 μeq. of the reagent, the extraction by 2 ml. of *n*-butanol was somewhat reduced to 97%.

Shaking Time.—With a large amount of the reagent, it is to be expected from the extraction rate that the equilibrium can be readily achieved by directly agitating both phases without heating. Therefore, an aqueous acetate system containing 1 meq. of the reagent was mixed with each 5 ml. portion of *n*-butanol or benzene. The effect of the shaking time on the extractability is given in Fig. 8, where the equilibrium extraction can not be attained even by a shaking of up to 2 hr. Because it requires a longer time for equilibration, the formation of the extractable 8-hydoxyquinolate in an aqueous system by heatnig should be followed by the extraction.

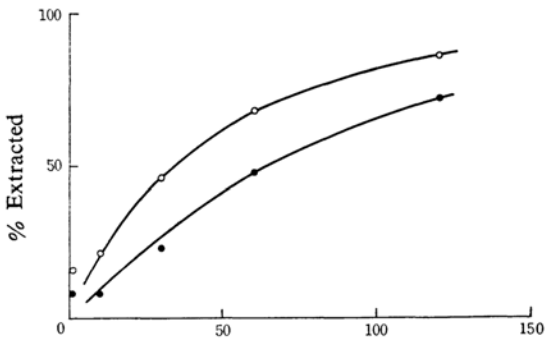

Fig. 8. Effect of shaking time on the extraction
○ *n*-Butanol
● Benzene

It may also be concluded that the complex formation in the aqueous phase is the limiting step in this separation method.

The Presence of a Water-Miscible Solvent.—Although the benzene extraction was sufficient for the extraction of ruthenim, the enhancement of extractability was recognized with *n*-butanol as the extracting solvent and, morever, with *n*-propanol present in an aqueous system.

The fairly water-miscible solvents seemed to be efficient for the formation and subsequent extraction of 8-hydroxyquinolate. It has been discussed now, in a chelate extraction system, a good extraction can be attained by the effect of a mixed solvent.[27,28] On the basis of these considerations, further investigation was carried out with such solvents to produce some different media for the formation of 8-hydroxyquinolate. First, the 8-hydroxyquinolate was formed in 6.2 ml. of the aqueous solution containing 1 ml. of a water-miscible solvent, such as *n*-propanol, methyl cellosolve, ethylene glycol, dioxane and pyridine, and then the extraction was carried ont with 2 ml. of benzene. As is shown in Table IV, the percentage extraction is greater to a minor, but appreciable, extent in the presence of any of the solvents excepting pyridine, than in their absence. No simple relation can be found between the solvent character and the extractability, as the extractability does not reach its highest point even with dioxane, which has the lowest

TABLE IV. EFFECT OF THE PRESENCE OF WATER MISCIBLE SOLVENT

Solvent	% Extracted in 2 ml. of benzene
n-Propanol	98.5, 99.5*
Methyl cellosolve	97.0
Ethylene glycol	97.9
Dioxane	98.0
Pyridine	49.3
None	96.9, 99.0**

* With 2 ml. of *n*-propanol.
** With 5 ml. of benzene.

dielectric constant among the solvents. In the presence of *n*-butanol, the highest result was attained, and by the later *n*-butanol extraction, the extractability might be enhanced remarkably: a combination of 2 ml. of *n*-propanol and 5 ml. of *n*-butanol resulted in the 99.9% extraction of ruthenium.

Back Extration.—To examine the conditions for the back extraction of ruthenium, a 5 ml. aliquot of the benzene containing 8-hydroxyquinolate was shaken with an equal volume of aqueous mineral acids or an aqueous solution of some organic reagents. The results are given in Table V and Fig. 9. The back

TABLE V. BACK EXTRACTION OF RUTHENIUM

Back Extractant	Shaking time, min.	% Back Extracted
pH 4.5 acetate buffer	1	1.2
1 M HCl	1	1.5
11.6 M HCl	10	95.0
1 M HNO_3	1	1.5
0.5 M H_2SO_4	1	1.4
9 M H_2SO_4	10	97.0
0.1 M EDTA	10	4.3
0.3 M Oxalic acid	10	2.8
0.3 M Sodium citrate	10	1.3
0.1 M Hydroxylamine	10	1.5

27) N. Suzuki and T. Kato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1148 (1959); *Sci. Rept. Tohoku. Univ., Ser. I*, **43**, 152 (1959).
28) C. L. Luke and M. E. Campbell, *Anal. Chem.*, **26**, 1778 (1954).

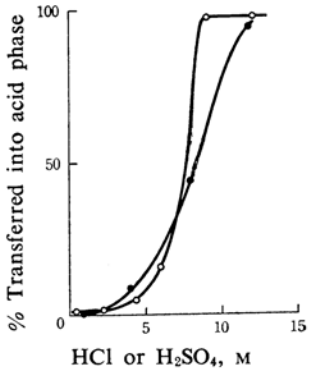

Fig. 9. Stripping of ruthenium by hydrochloric and sulfuric acid.
Shaking time: 10 min.
● HCl
○ H_2SO_4

extraction of ruthenium was not attained appreciably with the various back extractants listed in Table V except for concentrated mineral acid.

8-Hydroxyquinolate, once formed, retains its extractable property, even in a range of extremely low pH values where the excess reagent is transferred into the aqueous phase as a protonated form of 8-hydroxyquinoline, H_2Ox^+.[29] Washing a benzene extract with 1 N mineral acid, almost all the excess reagent can be removed with as little a loss of ruthenium as 1.5%. 8-Hydroxyquinolate is released by contact with more concentrated hydrochloric or sulfuric acid, and 95% of the ruthenium is found in concentrated hydrochloric acid after 10 minutes' agitation.

The Application of Solvent Extraction. — Ruthenium(IV) 8-hydroxyquinolate is greenish-yellow in color. The absorption spectrum of the benzene solution, shown in Fig. 10, is characterized by an intense peak at 437 mμ and a broad maximum at about 700 mμ in the visible range.[30] The colorimetric determination of a minute amount of ruthenium can be attained directly in the organic extract; the experimental conditions for this purpose will be described in detail elsewhere.

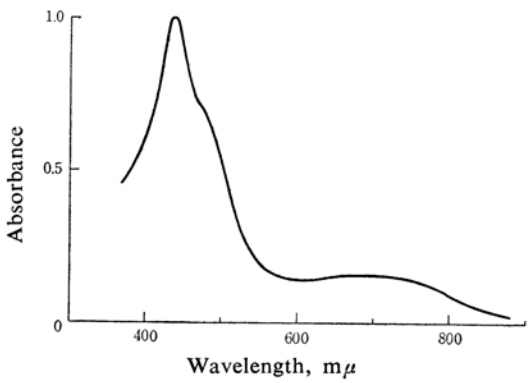

Fig. 10. Absorption spectrum of ruthenium(IV)-8-hydroxyquinolate in benzene extract.
Ru: 32 μg.
Solvent: 10 ml. of benzene

Next, the elements in mixed fission products were tested for their extractable properties by this method. Each pure nuclide in a carrier-free state[31] was subjected individualy to the experimental procedure; extraction with 5 ml. of benzene from an aqueous acetate solution of pH 4 containing 1 meq. of the reagent, and back extraction with an equal volume of 1 N nitric acid. Table VI shows 86.6% of the original zirconium-niobium-95 is accompanied by ruthenium-106 in the benzene extract but is completely separated by the following acid washings. The decontamination from the nuclides tested is complete. Ruthenium-103, 106 of a high radiochemical purity can be obtained from the mixed fission products by this extraction method.

Table VI. Behavior of some fission product nuclides

Nuclide	% Found in benzene extract	% Found in 1 N nitric acid*
Cs-137	1.0	94.3
Ce-144	1.8	95.5
Zr-Nb-95	86.6	98.9
Sr-90	0	—
Y-90	0.7	—
Ru-106	99.0	1.5

* Expressed as a percentage of c. p. m. found in acid phase to that contained in orginal benezene extract.

Summary

The solvent extraction behavior of ruthenium(IV) with 8-hydroxyquinoline has been investigated in detail using ruthenium-106 as a tracer.

The complex formation in the aqueous phase is fairly slow and is the limiting step in the procedure, but it can be enhanced by heating. Complete extraction is attainable with *n*-butanol, benzene and other organic solvents after 8-hydroxyquinolate has been formed by one hour's heating at 60°C with the excess reagent in an aqueous acetate medium of pH 4~6. *n*-Propanol, especially when combined with *n*-butanol, is an efficient extraction solvent. The presence of ammonium salts, organic

29) S. Lacroix, *Anal. Chim. Acta*, **1**, 260 (1947).

30) For measurement, an auto-recording spectrophotometer, Model EPS-2, made by the Hitachi Co., Japan, was employed.

31) Imported from the Radioisotopes Division of Oak Ridge National Laboratory, U. S. A.

acids or their salts causes interference. 8-Hydroxyquinolate, once formed, remains extractable even at very low pH values. The stripping of ruthenium from the benzene extract is accomplished by contact with concentrated hydrochloric acid.

This solvent extraction is applicable to the colorimetric determination of minute amounts of ruthenium and to the isolation of ruthenium activities in mixed fission products.

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