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USE OF ION EXCHANGE RESINS TO CONCENTRATE RADIONUCLIDES FOR SUBSEQUENT ANALYSIS

B. Kahn
E. R. Eastwood
W. J. Lacy

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USE OF ION EXCHANGE RESINS TO CONCENTRATE RADIONUCLIDES FOR SUBSEQUENT ANALYSIS*

Bernd Kahn, Edwin R. Eastwood and William J. Lacy**

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ABSTRACT

A procedure for determining low levels of radionuclides in water has been developed. Radioactive cesium, strontium, cerium, and cobalt are concentrated from one liter samples of river water by cation exchange resins and then purified by standard radiochemical techniques. The radionuclides and their carriers are absorbed on resin from 0.001 M hydrochloric acid solutions and then eluted with 20-25 ml of strong hydrochloric or nitric acid. The quantity of resin needed depends on the amount of calcium in the water. Sensitivity of detection has been increased by this method from approximately 10^{-6} to 10^{-8} μc/ml. The method has been utilized to perform radiochemical analyses of ORNL Settling Basin and Clinch River waters.

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INTRODUCTION

The minimum concentration of beta emitting radionuclides in water which is detectable using routine procedures is approximately 10^{-6} microcuries/ml. This minimum value is imposed by the use of a 10 ml sample volume and counting conditions which include 10% geometry, a counter background of approximately 20 counts/min and a 20-minute counting time. Detection sensitivity can be increased 100 fold by using 1 liter samples, and another 10 fold by improving counting conditions. The subject of this study is the feasibility of using large sample volumes for more sensitive radiochemical analysis.

Since radiochemical analytical procedures which have been well developed and tested usually require small sample volumes, most are carried out in 50 ml centrifuge tubes. Therefore, it was considered more simple to reduce the volume of the initial sample and then utilize these same procedures rather than to develop entirely new ones. Such concentration is routinely achieved by evaporation,[1] a very slow process and one subject to losses of radioactivity, and by coprecipitation,[2,3] in which the separation of the radionuclide from its nonisotopic carrier is crucial. Considered here is the alternate approach of absorbing the radionuclide from a liter sample of water on an ion exchange resin,[4,5] and eluting it with a small volume of acid. The radionuclide can then be recovered from the acid by the usual radiochemical techniques.

This concentration procedure is applicable only to ionic species, and specifically to those which can be readily absorbed on resins and eluted from them. Quantitative absorption and elution is not necessary

because an isotopic carrier is added to the sample and weighed at the end of the procedure. However, complete interchange of carrier and radionuclide in the sample is necessary.

The absorption, elution, and subsequent radiochemical analysis of cesium, strontium, cerium, zirconium, and cobalt were studied using radionuclides of these elements. Suitable resin column dimensions, flow rates, and eluant volumes were determined. Following the development of the procedures, analyses were made of ORNL waste streams.

PROCEDURE

The water samples used in this study were taken from the Clinch and Tennessee Rivers. The salt content of the waters are given in Table I. Immediately after sampling, 1 ml 1 M hydrochloric acid was added per liter to prevent hydrolysis and adsorption on the glass container of the radionuclides.

The radioactive tracers cesium-137, strontium-89, cerium-144, zirconium-95, and cobalt-60 were obtained from the Operations Division, Oak Ridge National Laboratory. They were counted with a well-type sodium iodide gamma scintillation counter or with a mica end-window Geiger-Muller beta counter. Approximately 20 mg of their respective carrier (usually nitrate salts) was added to each liter sample.

The cation exchange resins used were Dowex-50 (50-100 mesh, 5 meq/g, H^+ cycle, 90% moisture, styrene type) and IR-120 (20-50 mesh, 4 meq/g, Na^+ cycle, 85% moisture, sulfonic acid type). They were washed with dilute hydrochloric acid and with distilled water, and were then placed in 1.0

TABLE I

Chemical Analysis of Water Samples

Substance	Concentration in mg/liter	
	Clinch River	Tennessee River
Sodium	2.6	8
Potassium	1.4	1.5
Calcium	23	28
Magnesium	4	3.4
Iron	0.05	0.05
Sulfate	18	21
Chloride	20	17
Nitrate	2.3	0.9
Carbonate	46	44
Silicon dioxide	2	1.0
Total Dissolved Solids	77 ?	122

cm i.d., glass columns.

Experimental studies made were the following:

1) Radionuclide absorption and resin capacity. Water samples containing known amounts of individual carriers and tracers were passed through the resin columns until the effluent activity and hardness began to increase rapidly, indicating breakthrough. Thus the capacity of the resin for the particular element was determined. The influent and effluent activity before breakthrough were compared for a number of different flow rates and for different amounts of resin to determine the fraction of radionuclide leaking through the column. Calcium being the most abundant cation in water, and therefore likely to affect the absorption of the radionuclides, Versene hardness tests[6] were made on influent and effluent samples. All tests were duplicated for both resins and both waters.

2) Elution. Resin columns containing the absorbed radionuclides were leached with 6 M hydrochloric acid, 3 M nitric acid, concentrated nitric acid, or 0.1 M nitric-oxalic acids, to compare the effectiveness of each for eluting the radionuclides. Acid volumes needed for effective elution were determined also. The fraction of radionuclide eluted was obtained by counting aliquots of the leach acids and the resin, and by means of activity and material balances for the absorbed tracers and carriers.

3) Radiochemical analysis with tracers. One liter samples of the river waters, containing known amounts of individual tracers and carriers, were passed through 5.0 g (moist weight) of Dowex-50 resin at 5 ml/min.

Tracers and carriers were then eluted, at 0.5 ml/min., with the following:

cesium - 20 ml 6 M hydrochloric acid

strontium - 40 ml 14 M nitric acid

cobalt - 25 ml 3 M nitric acid

cerium - 25 ml 3 M nitric acid.

Cesium was separated from the non-radioactive contaminants (most important being the other alkalies) by precipitating cesium silicotungstate from cold 6 M hydrochloric acid, and recovered by dissolving that precipitate in sodium hydroxide and precipitating the perchlorate.[7] Strontium was separated from calcium and other contaminants by adding 35 ml fuming nitric acid to the nitric acid eluant and cooling to precipitate strontium nitrate. The precipitate was washed carefully with two 20 ml portions of 1:1 absolute alcohol-ether solution, dissolved in 5 ml water, and again precipitated as the nitrate with 20 ml fuming nitric acid. The strontium was redissolved in water and then precipitated as the oxalate.[8] Cerium was precipitated in turn as the fluoride, the hydroxide, and the oxalate.[9] Cobalt was recovered by precipitating first the hydroxide, then potassium cobaltinitrite, and then the 1-nitroso-2-naphthol salt.[10] The final precipitate in each case was weighed to determine carrier loss and then counted. The count rate was corrected for loss of tracer (equal to the loss of carrier), and compared to the amount of activity added to the original sample.

4) Radiochemical analysis of effluent water. Low level effluent waste from Oak Ridge National Laboratory was analyzed by procedures

described in the previous section. For comparison, the radionuclides were also concentrated by coprecipitation, cesium being carried on potassium cobaltinitrite,[3] strontium on calcium carbonate,[2] and cerium and cobalt on ferric hydroxide. Concentration by either procedure was followed by the same radiochemical analysis.

RESULTS AND DISCUSSION

The acid added to the water prevented the adsorption of cesium, strontium, cerium, and cobalt on glass, but did not prevent the adsorption of zirconium tracer or the settling out of zirconium carrier. This behavior indicated the non-ionic character of at least some of the zirconium in water, hence no further studies were made with the element.

The volumes of water that could be passed through the resin columns before the breakthrough occurred are given in Table II. Since 5 g of Dowex-50 and 2.5 g of IR-120 are sufficient for absorbing the radionuclides studied from liter volumes of water, these weights were used for all elements. The flow rate of 5 ml/min was suitable and caused little leakage of the radionuclides in the Dowex-50 column. The higher leakage in the IR-120 column is attributable to its larger resin particle size and shorter column length. Breakthrough of calcium ions occurred almost simultaneously with that of cesium, strontium, and cobalt: the limited capacity of the resin for these three radionuclides suggested that the radionuclides (and their carriers) were displaced at the breakthrough point by the relatively large amounts of calcium. This

TABLE II

Absorption of Radionuclides on Resin Columns
Radionuclides Plus Carriers Absorbed From
River Water

Cation	Resin	Resin Weight (g)	Water Volume (ml)	% Absorbed	Breakthrough Volume (ml)
Cesium	Dowex-50	5.0	1000	99.97 ± 0.01	1200
	IR-120	5.0	2000	99.93 ± 0.01	2500
	IR-120	2.5	1000	98.6	1000
Strontium	Dowex-50	2.5	1000	84. ± 1.	
		3.0	1000	93. ± 1.	
		3.5	1000	97. ± 1.	
		4.0	1000	99.7 ± 0.1	
		5.0	1000	99.9 ± 0.1	1400
	IR-120	2.5	1000	97.3 ± 0.3	1900
	IR-120	3.5	2000	97.4	2500
	IR-120	5.0	1000	98.8	
	IR-120	5.0	2000	98.7	2500
Cerium	Dowex-50	5.0	1000	99.98 ± 0.02	
		5.0	3000	99.98 ± 0.02	>3000
	IR-120	2.5	1000	99.99 ± 0.01	
	IR-120	2.5	3000	99.98 ± 0.01	>3000
Cobalt	Dowex-50	5.0	1000	99.8 ± 0.1	1500
	IR-120	2.5	1000	97.4 ± 1.4	1600
Zirconium	Dowex-50	5.0	1000	99.7 ± 0.1	2000
	IR-120	2.5	1000	99.8 ± 0.1	1000

was indicated further by increasing the calcium concentration in water from 23 to 46 and 92 mg/liter, the breakthrough volume for cesium decreasing from 1200 to 900 and 400 ml, respectively. An exception to this behavior was provided by cerium, (a trivalent ion) which was absorbed readily even on a resin saturated with calcium.

The fractions of absorbed radioactivity eluted by the various acids are given in Table III. Acids were chosen which would give a reasonably complete recovery of the radionuclides in a volume of 20-40 ml, and which would be most suitable for the subsequent chemical separations. By combining the fraction retained as listed in Table II with the fraction eluted as listed in Table III, the fraction of cesium recovered with the eluant listed in the previous section is 99.9%, and the strontium, cerium, and cobalt recovered are 99.2%, 99.8%, and 99.7%, respectively.

The tracer activity found in liter samples by the combined concentration and radiochemical procedures are compared in Table IV with the activity added to the samples initially. Agreement is within the experimental error of the procedure, indicating good interchange of carrier and tracer and the absence of interfering stable elements in the final precipitate (unless, by chance, the errors from these cancelled each other.)

After obtaining satisfactory results for the tracer studies, the procedures were used to determine the four radionuclides in the effluent samples listed in Table V. The settling basin contains undiluted laboratory effluent having sufficient activity to permit

TABLE III

Elution of Radionuclides From Resin Columns

Radionuclides Plus Carriers Absorbed
On Resin Columns From River Water

Cation	Resin	Resin Weight (gm)	Eluant Acid	Acid Concentration (Molarity)	Acid Volume (ml)	% Eluted
Cesium	Dowex-50	5.0	HNO_3	3	15	99.93
			HCl	6	12	99.98
			HCl	6	20	99.98
	IR-120	2.5	HCl	6	15	99.6
		5.0	HNO_3	3	30	99.98
			HCl	6	30	99.98
			HNO_3	16	30	99.2
Strontium	Dowex-50	2.5	HNO_3	14	40	99.6
			HNO_3	16	40	97.8
		3.0	HNO_3	14	25	97.5
		3.5	HNO_3	14	25	97.3
		4.0	HNO_3	14	30	98.8
			HNO_3	14	40	99.96
		5.0	HCl	6	20	96.8
			HNO_3	16	20	96.6
			HNO_3	16	35	98.7
			HNO_3	16	40	98.3
			HNO_3	14	40	99.3
			HNO_3	14	35	99.3
			HNO_3	14	25	91.2
	IR-120	2.5	HNO_3	16	20	71.0
		3.5	HNO_3	16	20	79.0
		5.0	HNO_3	3	20	87.1
Cerium	Dowex-50	5.0	HNO_3	3	25	99.8
			HNO_3	3	20	98.7
			HCl	6	20	98.9
	IR-120	2.5	HNO_3	3	20	46
			HNO_3	3	30	68
			HNO_3	16	20	29
			HCl	6	20	98.9
			HCl	6	30	79

TABLE III
(Continued)

Cation	Resin	Resin Weight (gm)	Eluant Acid	Acid Concentration (Molarity)	Acid Volume (ml)	% Eluted
Cobalt	Dowex-50	5.0	HNO_3	3	25	99.9
			HNO_3	16	25	96.3
			HCl	6	25	99.7
	IR-120	2.5	HNO_3	3	25	98.0
			HCl	6	25	99.3
Zirconium	Dowex-50	5.0	HNO_3	3	25	84.7
			HCl	6	20	93.3
	IR-120	2.5	HNO_3	16	25	52
			HCl	6	20	96.8
			HCl	6	25	98.5
	Dowex-50	5.0	$H_2C_2O_4$-HNO_3	0.1	25	49.0

TABLE IV

Tracer Study of Analytical Methods

Substance	Added mg	Recovery %	Activity Added c/m	Activity Recovered (corrected for carrier recovery) (c/m)	% Deviation
Cesium	18.6	54 ± 1	92,810 ± 510 γ	91,280 ± 4400 γ	-1.6
Strontium	20.5	60 ± 2	7,740 ± 140 β	7,650 ± 110 β	-1.2
Cerium	15.7	83 ± 1	23,270 ± 150 γ	23,830 ± 630 γ	+2.4
Cobalt	11.2	65 ± 1	161,000 ± 2,500 γ	157,000 ± 9,800 γ	-2.5

TABLE V

Activity in ORNL Effluent

Sample	Substance	Count Rate Ion Exchange c/m/ml	Count Rate Precipitation c/m/ml	Activity* μc/ml
Settling Basin	Gross β	34 ± 1	[illegible]	[illegible]
	Cs β	10.3 ± 0.2	10.6 ± 0.2	6.7×10^{-5}
	Sr β	7.24 ± 0.04	--------	5.4×10^{-5}
	Rare Earth β	15.1 ± 0.5	15.4 ± 0.2	5.7×10^{-5}
	Co β	0.29 ± 0.03	0.34 ± 0.04	0.4×10^{-5}
Clinch River Mile 4.6	Gross β	0.1		
	Cs β	0.026 ± 0.002	0.026 ± 0.003	17×18^{-8}
	Sr β	0.009 ± 0.001	0.008 ± 0.001	6×10^{-8}
	Rare Earth β	0.021 ± 0.001	0.019 ± 0.002	8×10^{-8}
	Co β	0.008 ± 0.003	0.008 ± 0.001	9×10^{-8}

* Ratio of counts/disintegrations for samples counted on 2nd shelf of G-M Counter is:

Cs-137: 7%
Sr-90 : 6%
Ce-Pr-144: 12%
Co-60 : 4%

approximate comparison between concentrated and unconcentrated samples, while the radioactive effluent at Clinch River Mile 4.6 is so diluted with Clinch River water that no activity can be detected in unconcentrated samples. The values obtained for the settling basin from concentrated samples compare favorably with values found previously with unconcentrated samples, but are much more precise. The results for Clinch River Mile 4.6 indicate definitely that cesium, strontium, cerium, and cobalt are present. The same values were obtained whether concentration was by ion exchange or by coprecipitation. In the case of strontium, coprecipitation could not be used for the settling basin sample, presumably because the presence of sequestering agents prevented the precipitation of calcium carbonate.

CONCLUSION

The concentration and subsequent radiochemical analysis of cesium, strontium, cerium, and cobalt in river water by ion exchange was found to be feasible. The concentration method is simple and requires little attention. The sensitivity of the method, with 1 liter samples and ordinary beta counting equipment, is approximately 10^{-8} microcurie/ml.

The quantity of resin needed for concentrating radionuclides from a given sample volume depends on the calcium concentration in the sample, hence more resin than was used in these experiments may be required for very hard waters. Larger volumes of water may be processed by using more resin or by possibly complexing the calcium ion so that it will not be absorbed on the resin. When analyzing water containing very low concentrations of radionuclides, it is desirable to process blanks to eliminate the error caused by the use of slightly contaminated reagents.

It is believed that with proper preparation of the sample and ion exchange resins, the concentration procedure may be applied to a large number of radionuclides.

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