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SEQUENTIAL ANALYSIS OF RADIONUCLIDES
IN HEAVY WATER MODERATOR

Savannah River Laboratory

Aiken, South Carolina

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SEQUENTIAL ANALYSIS OF RADIONUCLIDES
IN HEAVY WATER MODERATOR

by

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ABSTRACT

A method was developed for determining the following seventeen gamma-emitting radionuclides in moderator samples: Ru¹⁰³, Ru¹⁰⁶, I¹³¹, I¹³³, Zr⁹⁵, Nb⁹⁵, Zr⁹⁷, Nb⁹⁷, Np²³⁹, Mn⁵⁶, Cr⁵¹, Ce¹⁴¹, Ce¹⁴³, Sr⁹¹, Sr⁹², Ba¹⁴⁰, and Na²⁴. The radionuclides are separated sequentially into six groups by solvent extraction and ion exchange. The activities of each fraction are determined by gamma counting and gamma spectrometry. Average recoveries from seven synthetic samples that contained ten representative radionuclides were 89 to 114% with an average material balance of 96%. Analyses of reactor moderator samples showed good agreement between the sequential method of analysis and individual analyses of the radionuclides.

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INTRODUCTION

The radionuclidic composition of heavy water moderator in reactors at the Savannah River Plant must be determined to establish the sources of fission and activation products and to support studies of corrosion kinetics of the moderator system and the reactor components. This moderator is continuously purified by ion exchange resins and hence has a high degree of purity. The precision of the analysis of each radionuclide must be 10 to 30%, depending upon the concentration of the radionuclide.

Published methods for separating and determining individual radionuclides are adequately precise, but require excessive time. Instead of separating the radionuclides, the complex gamma spectrum of moderator gamma activity can be partially resolved into its components by a stripping technique, but the spectrum is too complex for reliable computation. Data obtained by the stripping technique often show large (100% or greater) discrepancies from those that are obtained by methods for determining individual radionuclides. A rapid method was therefore required to separate the radionuclides into groups so that all nonvolatile radionuclides present in significant abundance could be reliably determined by gamma counting and gamma spectrometry.

SUMMARY

A method was developed for determining seventeen gamma-emitting radionuclides in heavy water from reactor moderator systems. The radionuclides are sequentially separated into six groups by solvent extraction and ion exchange and then measured by gamma counting and gamma spectrometry:

- $\text{Ru}^{103-106}$ are oxidized with NaOCl , extracted into CCl_4 , and measured by direct gamma counting of the CCl_4 extractant.
- I^{131} and I^{133} are reduced with N_2H_4 , extracted into xylene, and measured by gamma spectrometric analysis of the xylene extractant.

- Zr^{95} - Nb^{95} , Zr^{97} - Nb^{97} , and Np^{239} are extracted with di(2-ethylhexyl)phosphoric acid (HDEHP) in hexane and measured by gamma spectrometric and decay analyses.
- Mn^{56} , Cr^{51} , and $\text{Ce}^{141-143}$ are removed by adjusting the remaining aqueous phase to pH 2-6 and passing it through an ion exchange column of hydroxide-form anion resin. The radionuclides are determined by combining gamma spectrometric and decay analyses.
- Sr^{91-92} and Ba^{140} are separated by passing the effluent and washes from the first column through a second column, which contains carbonate-form anion resin, and are determined by gamma spectrometry and decay.
- Na^{24} , the only radionuclide in the effluent and wash from the second column, is measured by direct gamma counting of an aliquot of the combined effluent and wash.

When synthetic samples were analyzed, 89 to 114% of each radionuclide was detected with a relative standard deviation of 4 to 17%. Results from independent analyses showed good agreement with those from sequential analyses of reactor moderator samples.

DISCUSSION

The seventeen radionuclides listed in Table I are sequentially separated. Existing solvent extraction methods^(1,2,3) were adapted for the extractions. Xylene, instead of CCl_4 , is used to extract $\text{I}^{131-133}$ because xylene becomes the upper phase in the extraction sequence and prevents the volatilization of iodine in the aqueous phase. The ion exchange precipitation methods are similar to those of Glueckauf and Roberts⁽⁴⁾ and Samsahl.^(5,6)

TABLE I

Radionuclides Separated by the Sequential Method

<u>Radionuclide</u>	<u>Half Life</u>	<u>Fraction</u>
Ru ¹⁰³	40 d	Carbon tetrachloride
Ru ¹⁰⁶	1.0 y	
I ¹³¹	8.05 d	Xylene
I ¹³³	21 h	
Zr ⁹⁵	65 d	HDEHP
Nb ⁹⁵	35 d	
Zr ⁹⁷	17 h	
Nb ⁹⁷	72 m	
Np ²³⁹	2.35 d	
Mn ⁵⁶	2.58 h	Hydroxide-form resin
Cr ⁵¹	27.8 d	
Ce ¹⁴¹	32.5 d	
Ce ¹⁴³	33 h	
Sr ⁹¹	9.7 h	Carbonate-form resin
Sr ⁹²	2.7 h	
Ba ¹⁴⁰	12.8 d	Resin effluent and wash
Na ²⁴	15.0 h	

All counting is done with the samples in 20 x 150 mm test tubes placed in the 1-inch-diameter by 3-inch-deep well of a 5-inch NaI(Tl) crystal that is connected to a RCL 256-channel analyzer. The liquid or solid in the test tubes is diluted to 18.5 ml and mixed well before counting so the counting efficiency is that of a 3-inch right circular cylinder. The activity of each radionuclide is corrected for decay to 2 hours after sampling.

PROCEDURE

Moderator samples are taken in clean, new polyethylene bottles from well-flushed sampling lines. The time of sampling is indicated on the sample bottle label. Sampling schedules should be arranged so that only a minimum of time is lost between sampling and the start of analysis.

The radionuclides are separated and measured by the following procedure.

Sample Preparation before Solvent Extraction

Pipet an aliquot of the sample containing 10^4 - 10^5 gamma counts/(sec)(ml) into 2 ml of water in a 45-ml centrifuge cone (Corning #8062) with a screw cap. Substitute a polyethylene liner for the standard rubber liner of the cap to minimize reduction of ruthenium(VIII). Add 0.5 ml of ruthenium carrier solution (10 mg Ru/ml) and 0.1 ml of iodide carrier solution (10 mg I/ml). Make the solution basic with 12M KOH and add 5 drops in excess.

Ru¹⁰³⁻¹⁰⁶ Analysis

Add 10 drops of 5% NaOCl, mix, cap the cone, and allow to digest for one hour. Add 6 ml of purified CCl₄.⁽⁷⁾ Add 10M HNO₃ dropwise until the greenish solution turns yellow.

Mix the two phases for 3 minutes with a "Vortex"* mixer and allow the phases to separate. Remove the CCl₄ with a pipet and place it in a 20 x 150 mm test tube.

Repeat the CCl₄ extraction with a fresh 6-ml portion of purified CCl₄. Rinse the tube and pipet with 5 ml of purified CCl₄. Combine the extractants and rinse, and count the gamma activity of the solution to obtain the combined Ru¹⁰³⁻¹⁰⁶ activities.

I¹³¹ and I¹³³ Analyses

To the aqueous phase from the CCl₄ extractions, add 6 ml of o-xylene, 2 ml of 16M HNO₃, and 0.1 ml of 10M N₂H₄. Mix the two phases for one minute, allow them to stand 15 minutes, and mix again for 5 minutes. Remove the organic phase with a pipet and place it in a 20 x 150 mm test tube.

*Product of Clay-Adams, Inc., New York, N. Y.

Repeat the extraction with a fresh 6-ml portion of o-xylene. Rinse the tube and pipet with 5 ml of o-xylene. Combine the extractants and rinse, and analyze by gamma spectrometry. Use the bin distribution method of Overman⁽⁸⁾, including the solution of linear simultaneous equations, to resolve the spectrum for I^{131} and I^{133} activities.

Zr⁹⁵-Nb⁹⁵, Zr⁹⁷-Nb⁹⁷, and Np²³⁹ Analyses

To the aqueous phase from the previous extraction add 4 drops of 3% H₂O₂ and 5 ml of 25% HDEHP in hexane. Mix the two phases for 3 minutes. Remove the organic phase and place it in a 20 x 150 mm test tube. Repeat the extraction with a fresh 5-ml portion of HDEHP. Rinse the tube and pipet with 5 ml of hexane, combine the extractants and rinse, and analyze by gamma spectrometry.

Use the bin distribution method⁽⁸⁾ in conjunction with the decay of short-lived radionuclides to resolve the activities of Zr⁹⁵-Nb⁹⁵, Zr⁹⁷-Nb⁹⁷, and Np²³⁹, as follows: First, resolve the Np²³⁹ and total Zr-Nb activities. Allow the Zr⁹⁷-Nb⁹⁷ activity to decay for 5 days, and recount. Calculate the Zr⁹⁵-Nb⁹⁵ activity. The difference in these counts is the Zr⁹⁷-Nb⁹⁷ activity.

Sample Adjustment before Ion Exchange

Place the aqueous phase from the HDEHP extraction under a heat lamp for about 30 minutes. If solids form after heating, add just enough water to dissolve them. To the solution add 0.5 ml of barium carrier solution (10 mg Ba²⁺/ml) and 0.5 of strontium carrier solution (10 mg Sr²⁺/ml). Add a few drops of metacresol purple to the solution, and adjust the acidity until the red solution turns yellow. This solution is used for the ion exchange portion of the scheme.

Mn⁵⁶, Cr⁵¹, and Ce¹⁴¹⁻¹⁴³ Analyses

Half fill a sintered-glass filtering crucible (Corning #32960-15C) with "Dowex" 2 (10% divinylbenzene), 200-400 mesh, hydroxide-form resin.* Place the crucible on a 500-ml suction flask having a rubber bulb for suction and a 25 x 150 mm test tube to catch the effluent from the resin column. Pass the sample through the resin at a flow of about 4 ml/min. Wash the tube containing the sample with five 3-ml portions of water;

*"Dowex" is a trademark of Dow Chemical Co.

pass the washes through the resin and collect them in the test tube with the effluent. Remove as much water as possible and transfer the resin to a 20 x 150 mm test tube.

Analyze the resin for Mn^{56} , Cr^{51} , and $\text{Ce}^{141-143}$ by gamma pulse height analysis, as follows: From the initial count, calculate the Mn^{56} activity. Allow two days for the decay of 6.0-hr $\text{Tc}^{99\text{m}}$ (which appears in this fraction, but is not determined in this scheme), and then count for Ce^{141} and Ce^{143} - Cr^{51} , whose photopeaks overlap. Allow 8 days for the decay of Ce^{143} , recount the resin, and calculate the Ce^{141} and Cr^{51} activities. From these counts, calculate the activity of Ce^{143} .

Sr^{91-92} and Ba^{140} Analyses

Half fill a second sintered-glass filtering crucible with "Dowex" 2 (10% divinylbenzene), 200-400 mesh, carbonate-form resin. Place the crucible on a suction flask with a clean 25 x 150 mm test tube to catch the resin effluent. Pass the feed effluent and washes from the hydroxide-form resin through this resin column. Wash the test tube and resin with five 3-ml portions of 0.01M Na_2CO_3 . Transfer the resin to a 20 x 150 mm test tube.

Analyze the resin for Sr^{91-92} and Ba^{140} by gamma spectrometry, as follows: Make an initial count of the resin and calculate the Sr^{91} and Sr^{92} activities.⁽⁸⁾ Allow the strontium radionuclides to decay for 5 days and recount the resin to determine Ba^{140} .

Na^{24} Analysis

Mix the combined effluents (including the washes) from the carbonate-form resin. Pour the solution into a 50-ml graduated centrifuge cone, measure the volume to the nearest 0.5 ml, and transfer 18 to 18.5 ml of the solution to a 20 x 150 mm test tube. Count the gamma activity of the solution to obtain the Na^{24} activity.

PRECISION OF THE METHOD

The precision of the method for ten representative radionuclides was determined by analyzing seven synthetic samples. The results are given in Table II.

TABLE II

Precision of Analyses of Seven Synthetic Samples

<u>Radionuclides</u>	<u>No. of Determinations</u>	<u>Avg % Recovery</u>	<u>Relative Standard Deviation, %</u>
Ru ¹⁰³	6	102	7
I ¹³¹	7	94	4
Zr ⁹⁵ -Nb ⁹⁵	7	114	9
Mn ⁵⁴	6	100	17
Ce ¹⁴¹	7	95	4
Sr ⁸⁵ -Ba ¹³³	7	89	10
Na ²²	7	100	9
Np ^{239(a)}	6	100	17
Material Balance	7	96 (overall)	3

(a) Not included in this series. Data from prior sample series..

Analyses by independent analytical methods confirmed sequential-scheme analyses of four samples of reactor moderator. Differences for Ru¹⁰³⁻¹⁰⁶, I¹³¹, I¹³³, and Np²³⁹ were less than 15%. Differences were 22% for Sr⁹¹, 24% for Na²⁴, 31% for Mn⁵⁶, and 35% for Sr⁹².

Comparisons were not made for Zr⁹⁵-Nb⁹⁵ and Zr⁹⁷-Nb⁹⁷, since only Zr⁹⁵ and Zr⁹⁷ were determined in the independent method, while the sequential scheme included the daughter activities. Calculation of Nb⁹⁵ and Nb⁹⁷ activities from the parent activities were questionable due to uncertainties in parent-daughter equilibria. Due to difficulties in the independent methods for Ce¹⁴¹⁻¹⁴³ and Ba¹⁴⁰, direct comparisons with the sequential scheme were not made for these radionuclides. Empirical examination of the data, however, indicated adequate agreement of the two methods for Zr⁹⁵, Zr⁹⁷, Ce¹⁴¹⁻¹⁴³, and Ba¹⁴⁰. Cr⁵¹ was found and determined in two of the moderator samples; however, no independent analysis was made for Cr⁵¹.

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