A Rapid Method for the Radiochemical Determination of ^{95}Zr - ^{95}Nb in Sea Water

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*A simple and rapid method is proposed for the determination of ^{95}Zr - ^{95}Nb in sea water. The method is based on the coprecipitation of ^{95}Zr - ^{95}Nb on lanthanum hydroxide followed by the extraction with 5% tri-*n*-butyl phosphate in toluene from 10 N hydrochloric acid solution. A high decontamination from other fission products was attained and the yield of ^{95}Zr - ^{95}Nb was larger than 99%.*

1. Introduction

The controlled release of the radioactive waste into the sea has been continuously a big research subject, receiving much attention both from scientific and social points of view. It is very important at present to establish the methods for determining radionuclides in sea water and marine environment in connection with this problem.

As to the determination of ^{95}Zr and ^{95}Nb in seaweed or sea water, Hampson¹⁾ and Das Gupta and Green²⁾ described a radiochemical procedure which was based upon coprecipitation on barium hexafluorozirconate and then on zirconium mandelate. Lai and Goya³⁾ of U.S. Naval Radiological Defense Laboratory modified the Hampson's procedure, giving a standard radiochemical method for the determination of these nuclides in sea water. The procedure of Lai and Goya, however, involves rather tedious steps of precipitation and scavenging and requires rather long time. It seems, therefore, desirable to establish more simplified and rapid method for the routine or many-sample analysis.

In this paper, an accurate and rapid method is proposed for the determination of ^{95}Zr - ^{95}Nb pair in sea water. The method is based on coprecipitation of ^{95}Zr - ^{95}Nb on lanthanum hydroxide followed by extraction with 5% solution of tri-*n*-butyl phosphate in toluene, and has revealed the high decontamination

from other fission products by a series of tracer studies.

2. Recommended Procedure

The following radiochemical procedures can be recommended being based on the results obtained by a series of experiments.

- (1) Take an appropriate amount of sea water sample in a beaker. Add 10 ml of concentrated nitric acid per litre of sea water*.
- (2) Add lanthanum nitrate (100 mg La) and zirconyl nitrate (5 μg Zr) as carriers.
- (3) Add a slight excess of ammonia to precipitate lanthanum hydroxide**. Decant and discard the supernatant solution.
- (4) Wash the precipitate with dilute ammonia water (1:100), centrifuge and discard the supernatant solution.
- (5) Dissolve the precipitate with 20 ml of hot 10 N hydrochloric acid.
- (6) Reprecipitate lanthanum hydroxide by adding a slight excess of ammonia, and centrifuge. Wash the precipitate with ammonia (1:100).
- (7) Dissolve the precipitate with 20 ml of hot 10 N hydrochloric acid.
- (8) Add small amount (about 100 mg) of hydroxylamine hydrochloride.
- (9) Extract zirconium and niobium in a

* When the sample is to be sent to the laboratory, it should be acidified with concentrated nitric acid immediately after the sampling.

** It is desirable to make precipitate under heating.

separatory funnel with 20 ml of 5% toluene solution of tri-*n*-butyl phosphate.

- (10) Scrub the organic layer with 20 ml of fresh 10 *N* hydrochloric acid, and discard the aqueous phase.
- (11) Take an aliquot of the organic layer and measure the activity. When the activity level is low, dry up the organic layer by careful evaporation in a counting dish and measure the activity with a low background counting apparatus.

3. Experimental

The recovery of ^{95}Zr - ^{95}Nb and the decontamination of the zirconium fraction from several other fission products at each precipitation and solvent extraction step were examined at least twice by the tracer method.

3.1 The sea water sample

The sea water was taken at the coast of Tokai, Ibaraki Pref. Its pH value and temperature were 7.8 and 12.5°C, respectively. It was acidified with concentrated nitric acid.

3.2 Reagents

All chemicals used were of the reagent

grade.

3.3 Measurement of radioactivity

A scintillation counter with a well-type NaI(Tl) crystal (1¼ in. × 2 in.) or a 400 channel γ -ray spectrometer made by Technical Measurement Corp. was used for the activity measurement. A G-M counter was employed for the β -counting of ^{90}Sr and ^{90}Y .

4. Results and Discussion

An appropriate amount of ^{95}Zr - ^{95}Nb , ^{90}Sr - ^{90}Y , ^{106}Ru , ^{131}I , ^{137}Cs , ^{144}Ce or $^{152+154}\text{Eu}$ was added as the tracer to 50 ml of sea water together with lanthanum and zirconium carriers, and percentage coprecipitation, percentage extraction and the over-all yield were obtained.

4.1 Determination of percentage coprecipitation

From the tagged solution, 4 ml was taken for the initial activity measurement (Let counting rate be a_0 cpm.). Another 40 ml was taken out of the rest and lanthanum hydroxide was precipitated according to Procedure (3). Four ml of the supernatant solution was taken for the activity measurement (Let counting rate be

Table 1 Recovery of some radionuclides

Radionuclide	Run	Percentage coprecipitation [ξ] (%)	Distribution ratio [D]	Percentage extraction [η] (%)	Over-all yield [ξ] (%)
^{95}Zr - ^{95}Nb	I	99.1	83.1	98.8	97.9
	II	99.3	75.3	98.7	98.0
^{144}Ce	I	99.8	0.0035	0.35	0.35
	II	99.8	0.0048	0.48	0.48
$^{152+154}\text{Eu}$	I	100.0	0.0027	0.27	0.27
	II	100.0	0.0025	0.25	0.25
^{106}Ru	I	96.0	0.00072	0.072	0.069
	II	95.8	0.0020	0.20	0.19
^{90}Y	I	100.0	0.001	0.1	0.1
	II	100.0	0.0006	0.06	0.06
^{137}Cs	I	1.40	0.0058	0.58	0.0081
	II	1.90	0.0030	0.30	0.0057
^{90}Sr	I	0.047	0.0024	0.24	0.00011
	II	0.089	0.0034	0.34	0.00030
^{131}I	I	3.25	26.0	96.3	3.13
	II	4.27	25.1	96.2	4.11

a_1 cpm.). The precipitate was treated according to Procedures (4) and (5), and the volume of the obtained hydrochloric acid solution was made to be 25 ml. The activity of 4 ml of the solution was then measured (Let be a'_1 cpm.). Percentage coprecipitation (ξ) was calculated by the following formula:

$$\xi = \left(1 - \frac{a_1}{a_0}\right) \times 100\% \quad (\text{when } a_1 < a'_1)$$

or
$$\xi = \frac{25}{40} \cdot \frac{a'_1}{a_0} \times 100\% \quad (\text{when } a_1 > a'_1)$$

The results are shown in the third column of Table 1.

4.2 Determination of percentage extraction

The labelled sample was treated following Procedures (3) to (8). From 20 ml of the obtained solution, 4 ml was taken for the activity measurement (Let counting rate be b_0 cpm.). When b_0 was small, an appropriate amount of the radioisotope was added. Ten ml was taken out of the rest in a separatory funnel, and shaken with 10 ml of 5% toluene solution of tri-*n*-butyl phosphate.

The activities of 4 ml of both the aqueous and organic layers were measured (Let counting rate be b_1 and b'_1 cpm, respectively.). Distribution ratio (D) and percentage extraction (η) were calculated by the following formulae:

$$D = \frac{b'_1}{b_1}$$

$$\eta = \left(1 - \frac{b_1}{b_0}\right) \times 100\% \quad (\text{when } b_1 < b'_1)$$

or
$$\eta = \frac{b'_1}{b_0} \times 100\% \quad (\text{when } b_1 > b'_1)$$

The results are shown in the fourth and fifth columns of Table 1.

4.3 Determination of the over-all yield

The over-all yield (ζ) can be readily calculated by the following formula:

$$\zeta = \xi \eta \times \frac{1}{100} \%$$

The values are shown in the last column of Table 1.

On the other hand, the over-all recovery of ^{95}Zr - ^{95}Nb was measured directly through the whole procedure by using 1 l of the sea water sample labelled with ^{95}Zr - ^{95}Nb of the activity ten times as high as the background, and found to be 99.3%.

As shown in Table 1, both recovery of ^{95}Zr - ^{95}Nb and decontamination from all nuclides tested are satisfactory except the decontamination from ^{131}I . Since the half-lives of iodine isotopes existing in the fission products, however, are rather short or very long and contamination is 3~5%, there is no significant influence of radioactive iodine to the determination of ^{95}Zr - ^{95}Nb in the fission products cooled for several ten days. Therefore no further treatment for decontamination from iodine was carried out.

The procedures were then examined by using fission products mixture, giving a high enough radiochemical purity of ^{95}Zr - ^{95}Nb in the final organic layer at the step (10). The decay curve of the organic layer fitted to the 65 day half-life of ^{95}Zr , and the extraction of ^{95}Nb together with ^{95}Zr was confirmed by the fact that no growth was observed in the decay curve. The γ -spectrum of the organic layer was in good concordance with that of ^{95}Zr - ^{95}Nb .

Finally the "addition test" experiments were carried out: To 1 l of the sea water sample, a known amount of fission products

Table 2 Result of the "addition test"

Run	Sample and the added radionuclides	Activity taken (cpm)	Activity found in the organic layer (cpm)	^{95}Zr - ^{95}Nb found [(b)-(a)] (cpm)	Recovery [(b)-(a)]/(c) $\times 100$ (%)
I	A. FP	16,442	11,112(a)		
	B. {FP	16,442	17,715(b)		
	^{95}Zr - ^{95}Nb	6,689(c)		6,603	98.7
II	A. FP	20,790	14,403(a)		
	B. {FP	20,790	20,723(b)		
	^{95}Zr - ^{95}Nb	6,357(c)		6,320	99.5

was added (sample A), and to another 1l of the sample water, a known amount of fission products and a known amount of ^{95}Zr - ^{95}Nb solution were added (sample B). Then separations were carried out with both samples in the same way as that mentioned above. The results are given in Table 2, showing the quantitative recovery of ^{95}Zr - ^{95}Nb by these procedures.

The present recommended procedure takes only 1 hour or less, includes no complicated or special technique and is accurate enough. The method seems, therefore, to be suitable for the routine or many-sample analysis of ^{95}Zr - ^{95}Nb .

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要 旨

海水中の ^{95}Zr - ^{95}Nb の放射化学分析法

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海水中の ^{95}Zr - ^{95}Nb を定量する簡単, 迅速な方法を考案した。試料水を硝酸酸性にし, 担体として硝酸ランタン (100 mg La) と硝酸ジルコニル ($5\text{ }\mu\text{g Zr}$) を加える。アンモニアを加えて水酸化ランタンを沈殿させ, ジルコニウムをこれに共沈させる。沈殿を10 N 塩酸に溶解後, リン酸トリ-*n*-ブチル (5%トルエン溶液) で ^{95}Zr - ^{95}Nb を抽出し, 有機相の放射能を測定する。おもな核分裂生成核種につき, トレーサーを用いて分離を検討したところ, ^{95}Zr - ^{95}Nb の共沈ならびに抽出における分離はいずれも定量的であり, かつ, 放射化学的純度も十分高いことが示された。