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A New Method for the Chemical Determination of Radium in Sea Water

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ABSTRACT

In a method for the determination of radium in sea water, radium is coprecipitated with calcium carbonate from the sea water and redissolved in dilute hydrochloric acid; it is then isolated by precipitation with barium rhodizonate, followed by separation on an ion exchange column. The radium compound is then dried and ignited on a platinum disk, and its radioactivity is measured with an α -spectrometer. The average recovery of radium from sea water is $94.0 \pm 2.0\%$.

Introduction. Previous analytical techniques for the determination of radium in sea water have been based on emanation or proportional counting methods (Faul, 1954; Rosholt, 1957). This paper reports the procedure and results of a new method for the separation and determination of radium in sea water by means of α -ray spectrometry.

Experimental. The following reagents were used: sodium rhodizonate, 0.2% in phthalate buffer solution; Dowex 50W-X8, 100-200 mesh; ammonium formate, 2M solution.

Radium-226, used as a tracer in the analytical procedure, was obtained from the United Kingdom Atomic Energy Authority. The Tracerlab RLD-1 Frisch Grid Chamber connected to a single channel pulse-height analyzer was used for α -spectrometry. The efficiency of radioactivity measurement at the energy level of 4.777 Mev for radium-226 was 33%.

Extensive experimentation resulted in the following procedure. An acidified seawater sample of about one liter was subjected to analysis. Calcium carbonate was precipitated from sea water by the addition of ammonium carbonate after the pH of the water had been adjusted to 7 with ammonium hydroxide. After

separation from the supernatant solution, the carbonate precipitate was dissolved in a minimum amount of dilute hydrochloric acid, and 10 mg of barium carrier were added. The pH was adjusted to 4 with acetate buffer solution, and 25 ml of 0.2% solution of sodium rhodizonate in phthalate buffer (pH 7) were added. After the solution had stood from 5 to 15 minutes, the pH was adjusted carefully to 1 by the addition of dilute hydrochloric acid solution. The precipitate of radium and barium was separated by filtration and dissolved in hot 4 N HNO₃ solution. The solution was evaporated, the residue was redissolved in nitric acid, and the concentration of the solution was adjusted to 0.4 N with respect to nitric acid. This solution was passed through the ion-exchange column at a flow rate of 1 ml/min. The resin bed consisted of a cation exchanger (Dowex 50W-X8, H⁺-saturated form, 100-200 mesh) in a glass column 20 cm long and 0.6 cm i.d.

The column on which the radium and barium were absorbed was washed with 50 ml of water and eluted with 2 N ammonium formate solution. The barium salt, which interferes with the α -counting, was separated from the radium and passed off in the first 60-ml portion of the effluent. Radium was subsequently eluted in the second 60-ml portion. The effluent was evaporated to dryness, and the residue was ignited with an infrared lamp. The inside of the vessel was rinsed thoroughly with about 5 ml of a mixed solution of 1 N formic acid and 1 M ammonium formate in order to redissolve the radium. This solution was transferred to a platinum disk (4 cm diameter), evaporated under infrared lamp, and ignited in order to expel ammonium formate. The α -ray activity of radium-226 (4.777 Mev) on the platinum disk was measured in an α -ray spectrometer.

The effectiveness of detection and separation of alkaline earth elements by means of potassium rhodizonate has been reported by Feigl (1958). Weiss *et al.* (1957, 1960, 1961) applied this reagent to the radiochemical separation of alkaline earth elements, but they did not examine fully the conditions required for the precipitation. Results of our detailed study on the conditions for precipitation of alkaline earth rhodizonates were as follows.

1. *Effect of the Hydrogen-ion Concentration.* Feigl (1958) reported that calcium rhodizonate was precipitated from only alkaline media, whereas strontium and barium rhodizonate were formed in neutral solution. Barium rhodizonate was precipitated even in a moderately acid medium.

The relationship between pH and the recovery of alkaline earth elements was studied in detail at room temperature. Buffer solutions with pH between 1-10, containing 20 mg each of calcium, strontium, and barium, were treated with a solution of sodium rhodizonate whose concentration was equivalent to four times the molar concentrations of the metallic ions. The solution was then diluted to 100 ml with distilled water. After standing for 15 minutes, the crystalline precipitate of rhodizonate was separated by centrifugation. The

recovery of calcium, strontium, or barium was determined by titration with 0.01 M EDTA following decomposition of the rhodizonate with hot nitric acid. The pH had no appreciable effect on the recovery of the metals, even when barium was associated with calcium or strontium; the same was true for strontium when it was associated with calcium. The recovery of the precipitate from the mixture was determined by titration with EDTA following separation of the metals by ion exchange (Tsubota and Kitano, 1960a). Each metal was precipitated with good recovery (Fig. 1). Maximum recoveries of barium and strontium were obtained at pH 4 and 8, respectively.

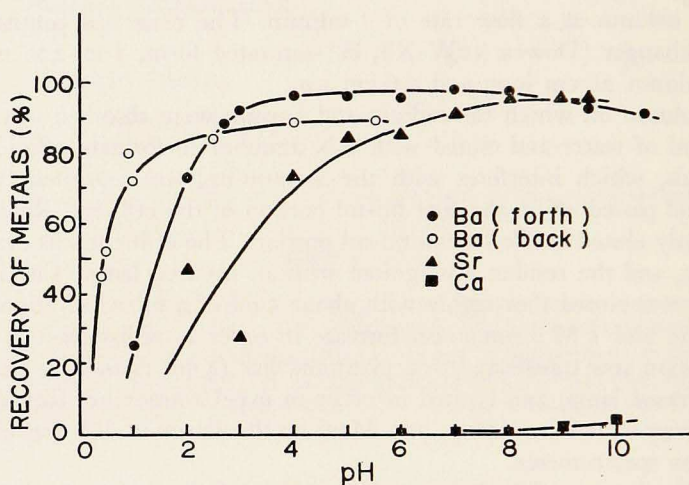


Figure 1. Relationship between recovery of metals and pH of solution.

Calcium or strontium rhodizonate formed at a high pH could be dissolved by lowering the pH. The dissolution curves for calcium and strontium were similar to the curves that showed formation of the precipitate with increasing pH. On the other hand, the dissolution curve for barium rhodizonate, with decreasing pH, shifted toward a lower pH. When the pH of the solution changed from 4 to 1, the color of barium rhodizonate changed from brown-red to purple-red. According to Feigl (1958), the chemical composition of the precipitate is supposed to be $\text{Ba}(\text{C}_6\text{O}_6\text{H})_2$. However, the rate of formation of barium rhodizonate was much faster at pH 4 than at pH 1; at pH 1 the recovery of the metal was too variable.

Decontamination of barium and radium rhodizonates from other alkaline earth rhodizonates was achieved by the so-called "back and forth" method. The mixed rhodizonates formed in a solution at pH 4 were allowed to stand for five minutes. The pH of the solution was then adjusted to 1 by the addition of dilute hydrochloric acid—a drop at a time while stirring. Under these con-

ditions, strontium and calcium rhodizonates dissolved while most of the barium rhodizonate remained in the solid form together with the coprecipitated radium.

The following buffer solutions were used; (a) pH 1 to 2, mixed solution of hydrochloric acid and sodium chloride; (b) pH 2 to 7, mixed solution of acetic acid and sodium acetate; (c) pH 6 to 9, hydrochloric acid and triethanolamine mixture; (d) pH 8 to 10, mixed solution of ammonium chloride and ammonium hydroxide, or a sodium borate and sodium hydroxide mixture.

2. *Amount of Reagent.* When the added reagent contained more than three to four times the amount of rhodizonate required to precipitate the combined alkaline earths in the sample, the recovery was almost constant. The relationship between recovery of metals and the amount of sodium rhodizonate is given in Fig. 2.

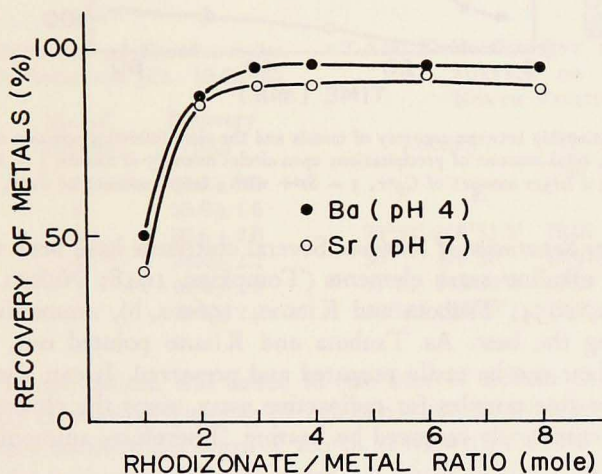


Figure 2. Relationship between recovery of metals and the amount of sodium rhodizonate.

3. The recovery of metals relative to the elapsed time following addition of the reagent was ascertained for solutions of pH 7 and for a rhodizonic acid concentration with a molar ratio of 4:1 to the metals present (Fig. 3). The effect of higher concentrations of calcium on the recovery of barium or strontium was also studied under the same conditions. A 0.1 m.mol solution of barium and strontium and a 10 m.mol solution of calcium were used respectively.

A minimum of five minutes was necessary to complete the precipitation of the metal rhodizonate. However, if a higher concentration of calcium was present in the solution, resulting in an increased total precipitation, the recovery of barium or strontium decreased if the sample was allowed to stand longer than 30 minutes following addition of the reagent.

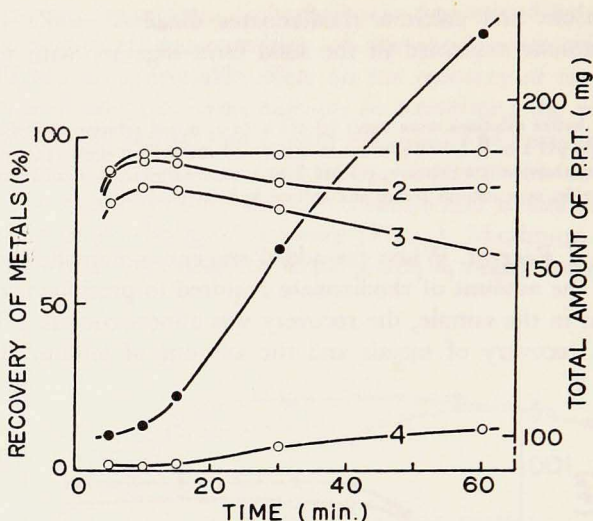


Figure 3. Relationship between recovery of metals and the time following addition of reagent. Solid dots, total amount of precipitation; open circle: recovery of metals. 1 = Ba^{2+} , 2 = Ba^{2+} with a larger amount of Ca^{2+} , 3 = Sr^{2+} with a larger amount of Ca^{2+} , and 4 = Ca^{2+} .

Ion-exchange Separation of Radium. Several elutriants have been used for the separation of alkaline earth elements (Tompkins, 1948; Nelson and Kraus, 1955; Honda, 1954; Tsubota and Kitano, 1960 a, b), ammonium formate probably being the best. As Tsubota and Kitano pointed out, ammonium formate elutriant can be easily prepared and preserved. It can also be used to prepare carrier-free samples for radioactive assay, since the eluting agent can be easily and completely removed by heating. Therefore, ammonium formate

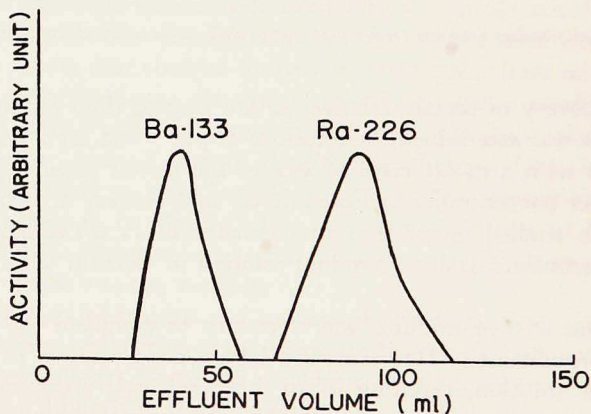


Figure 4. Elution curves of Ba^{2+} and Ra^{2+} .

was used as the elutriant to separate barium from radium, and to prepare pure or carrier-free samples of radium for α -counting.

In order to select suitable conditions for the separation, 10-mg aliquots of barium-ion containing barium-133 and radium-226 as tracers were adsorbed onto the ion-exchange column, described previously, and eluted with ammonium formate solutions of various concentrations. The effluents were collected in 5-ml fractions, the radioactivity of each fraction was determined, and elution curves were plotted. It was found that trace amounts of radium could be separated from 10 mg or more of barium with the use of 2 M ammonium formate as an elutriant (Fig. 4).

In each step of the analysis, recovery of radium is almost quantitative, but some losses may occur during the ignition process when the samples are prepared for radioactive assay.

TABLE I. RECOVERY OF RADIUM FROM NaCl SOLUTION (Cl: 19.00‰)

Ra added (g)	No. of Samples	Recovery (%)
9.0×10^{-9}	2	94.3 ± 2.0
4.5×10^{-10}	3	95.0 ± 1.6
4.5×10^{-11}	3	93.6 ± 2.0
9.0×10^{-12}	4	94.0 ± 2.2
4.5×10^{-13}	3	94.0 ± 2.0
Average		94.0 ± 2.0

TABLE II. CONTENT OF RADIUM IN SURFACE OF THE WESTERN NORTH PACIFIC.

Locality		Cl (‰)	Ra ($\times 10^{-13}$ g/l)
N	E		
29°58'	148°31.5'	19.02	1.0 ₀ ± 0.1
30°	139°50'	19.04	0.8 ₇ ± 0.1
37°52'	143°50'	19.09	0.8 ₇ ± 0.1
38°04'	148°02'	19.06	0.4 ₃ ± 0.06

Results. When radium was added to one liter of sodium chloride solution (Cl = 19‰) containing 400 mg of calcium-ion, the average recovery was 94.0%, with a standard deviation of 2.0%, as shown in Table I. Some results of analyses for radium-226 in sea water are given in Table II. So far as the radium content in sea water is concerned, many analytical values of radium have been reported; the radium content ranged from 3 to 30×10^{-14} g/l, the average value being 8×10^{-14} g/l (Pettersson, 1954; Koczy, 1957, 1958). Data for radium in western North Pacific waters are still rather scarce, but our results from analyses of radium in that area show the same order of magnitude as that given previously by Pettersson.

As shown by Weiss and Lai (1961), in the final residue (weighing 0.2 to 0.5 mg) the error due to self-absorption of α -particles is negligible. This method should be useful for analysis of radium in natural waters, and for the preparation of carrier-free samples for α -counting of radium.

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