

DETERMINATION OF BARIUM IN SEA WATER BY CATION-EXCHANGE SEPARATION AND ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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SUMMARY

A method is described for the routine determination of barium in sea water by graphite-furnace atomic absorption spectrometry. Barium is separated from the main sea-water cations by collection on a cation-exchange resin. The barium is extracted into nitric acid from a portion of the resin for injection into the pyrolytically-coated graphite furnace. The method is satisfactory for the low $\mu\text{g l}^{-1}$ levels of barium present in ocean water, with recoveries $\geq 99\%$ and a relative standard deviation of $< 5\%$.

Precise measurements of dissolved barium in sea water were reported on a world ocean scale by Chan et al. [1]. They used isotope-dilution mass spectrometry after the separation of barium by ion-exchange chromatography [1, 2]. Several investigators have tried to optimize conditions for direct determination of barium in sea water by graphite-furnace atomic absorption spectrometry (AAS) [3, 4] and atomic emission spectrometry [5, 6]. Direct-current plasma atomic emission spectrometry is also possible [7]. While these techniques are sufficiently sensitive and the background signal from the sea water matrix can be eliminated, none, with the possible exception of the last, appears to be useful for routine determination of barium in sea water. In graphite-furnace AAS the rapid degradation of pyrolytically-coated graphite tubes on repeated injection of sea water [4, 5] is a major impediment to its routine use. In this study, a method is described for ion-exchange separation of barium from the major sea salt components, followed by elution of barium in an acidic medium and subsequent determination by graphite-furnace AAS.

EXPERIMENTAL

Apparatus

A Varian AA-1275BD atomic absorption spectrometer equipped with a GTA-95 graphite furnace and programmable autosampler was used. The

barium hollow-cathode lamp (Instrumentation Laboratory) was operated at 8 mA. All measurements were made at the 553.6-nm barium line at a spectral band width of 0.5 nm (with decreased slit height). Pyrolytically-coated tubes (Le Carbone Lorraine) were used throughout. The furnace program is shown in Table 1. All absorbance readings were in peak-height mode. A Hamilton Microlab 1000 diluter was used for diluting. The ^{133}Ba activity was measured with a 2-in. pit crystal NaI scintillation detector (Canberra).

Sample preparation and reagents

Conditioning of the cation-exchange resin. Dowex 50W-X8 resin (200–400 mesh, H^+ -form; BioRad) was used throughout. After a few preliminary rinses, and discard of the floating fines, the resin was packed in a column, washed with 7.5 M hydrochloric acid (analytical grade) and rinsed with Milli-Q (Millipore) water until the pH was 5–6. The resin was converted to the ammonium form with 30% ammonia (analytical grade) and again rinsed with Milli-Q water to pH 5–6. The resin was dried at 60°C.

Batch experiments. The resin (1 g) was equilibrated overnight with 0.33 meq of the cation studied in 41 ml of solution. Cations were all used as their chlorides. Elements were determined in batch experiments by flame atomic absorption spectrometry (Varian AA-275 spectrometer). Ammonium chloride solutions used for column experiments were purified from barium on Dowex resin (NH_4^+ form) prepared as above.

Column experiments. For processing sea-water samples (≤ 120 ml), columns (13.4 mm i.d.) were filled with 2.5 g of the ammonium-form resin. Before the samples were applied, the resin was conditioned with 0.6 M ammonium chloride. Flow through the column was maintained at 1.5 ml min^{-1} with a peristaltic pump. After the major cations had been eluted (see below), the resin was washed chloride-free with Milli-Q water, dried at 60°C and homogenized for one hour in a Buchler vortex mixer. From this dry resin, small portions were weighed for subsequent exchange of barium into nitric acid in the autosampler cup.

Sample volumes of 100 ml were processed here, but this volume can be conveniently reduced, which allows a reduction of resin amount and eluant.

TABLE 1

Electrothermal program used for the determination of barium

Temp. (°C)	80	150	1200	1200	2500	2500	80
Time (s)	1.0	20	10	2.0	0.7 ^a	2.5 ^b	11
Argon (l min^{-1})	3	3	3	0	0	0	3

^aMaximum heating rate. ^bPeak-height absorbance measured during this period.

RESULTS AND DISCUSSION

Separation of barium from sea water

The effect of three counter-ions (H^+ , K^+ and NH_4^+) on the distribution coefficients, K_d , of barium and sodium, the main cation in sea water, was measured; K_d (in $ml\ g^{-1}$) is given by the ratio of the equivalents on the resin to the equivalents in solution, as deduced from the concentrations of Ba^{2+} or Na^+ added and those measured in solution after batch equilibration of the resin with 0.4 M hydrochloric acid. The results are shown in Table 2. It is clear that the ammonium form of the resin produces the best conditions for the separation of barium and sodium ions. Successful separation of the alkaline earth elements has been described by others, with ammonium malonate as the eluant [8]. In this investigation, satisfactory results for the separation of barium ions from a matrix containing Na^+ , K^+ , Ca^{2+} and Mg^{2+} as major cations were obtained with ammonium chloride as eluant.

Distribution coefficients for Ba^{2+} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ were obtained from separate batch experiments with 0–2 M ammonium chloride. The results are shown in Fig. 1. For each ammonium chloride concentration, selectivity coefficients, K_{B,NH_4} , were calculated:

$$K_{B,NH_4} = (B_R) (NH_4^+)^n / (NH_{4R})^n (B^{n+})$$

where () represents equivalent concentrations, B is the competing cation and R is the resin phase. Table 3 lists the arithmetic means of the selectivity coefficients for ammonium chloride concentration ranges that produced <5% relative standard deviation (RSD). These average selectivity coefficients can be used, within the corresponding ammonium chloride concentration range, to calculate K_d for any ammonium chloride concentration (see Appendix). These calculated K_d values are identified in Fig. 1.

The K_d value for barium ions in sea water is required to predict the breakthrough of barium when a sea-water sample is applied to the column. A batch experiment was done with an artificial sea-water solution with concentrations of the major cations close to their natural values (0.6 M Na^+ , 0.01 M K^+ , 0.01 M Ca^{2+} , 0.08 M Mg^{2+}). The Ba^{2+} content was 0.33 meq. This gave a K_d value for barium of $109\ ml\ g^{-1}$, a value that indicates that barium will have passed over 0.9 g of resin after the application of a 100-ml sea-water sample.

TABLE 2

Distribution constants of sodium and barium ions as a function of the counter-ion for a batch experiment with 0.4 M HCl (duplicate measurements)

Counter-ion	H^+	NH_4^+	K^+
$K_d(Na^+)$	18.5	10.7	8.2
	17.6	9.8	9.0
$K_d(Ba^{2+})$	484	795	664
	476	808	672

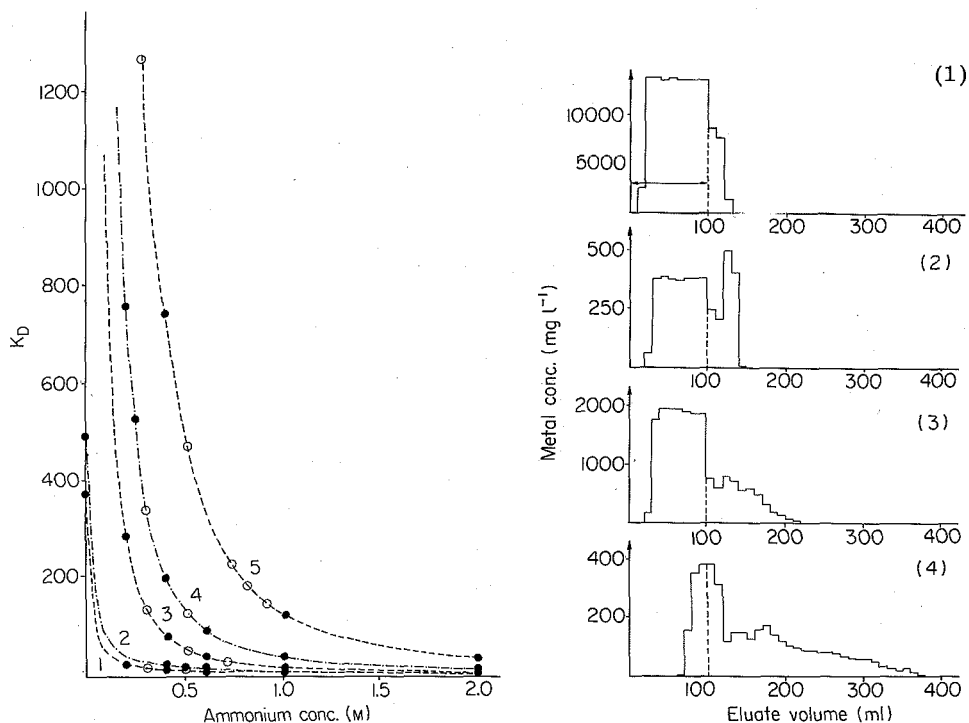


Fig. 1. K_d values vs. ammonium concentration: (1) Na^+ ; (2) K^+ ; (3) Mg^{2+} ; (4) Ca^{2+} ; (5) Ba^{2+} . (●) Experimental values; (○) calculated values, based on formulae in Appendix.

Fig. 2. Elution profiles: (1) Na^+ ; (2) K^+ ; (3) Mg^{2+} ; (4) Ca^{2+} . A 100-ml sea water sample was passed through a column containing 2.5 g of NH_4^+ -form resin; Na^+ , K^+ , Mg^{2+} , Ca^{2+} were eluted with 0.6 M ammonium chloride solution. The dashed lines indicate the end of the 100-ml sample introduction.

TABLE 3

Selectivity coefficients of Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} over various ammonium chloride concentration ranges

Ion	K_{B, NH_4}	RSD (%)	NH_4Cl (M)
Na^+	0.89	4.8	0.2–0.6
K^+	1.73	1.5	0.4–1.0
Mg^{2+}	24.4	3.6	0.2–1.0
Ca^{2+}	66.3	1.3	0.2–0.6
Ba^{2+}	241	1.3	0.2–2.0

From the distributions of K_d values as a function of ammonium chloride concentrations, a 0.6 M solution was selected as eluant, ensuring both maximum retention of barium and optimum elimination of Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The calculated column parameters and K_d values are given in Table 4. These parameters can be used to calculate that the peak maximum of Na^+ elutes at 21 ml, K^+ at 33 ml, Mg^{2+} at 89 ml and Ca^{2+} at 227 ml with 0.6 M ammonium chloride. Experimental elution profiles for the different cations are shown in Fig. 2, confirming the calculated data. In practice, the sea-water samples were eluted with 250 ml of 0.6 M ammonium chloride. The Ca^{2+} tail was eliminated with 20 ml of 1.0 M ammonium chloride.

Barium recovery. Aliquots (100 ml) of a natural sea-water sample were spiked with $0.5 \mu\text{Ci } ^{133}\text{Ba}$ and applied to columns containing 2.5 g of the ammonium form resin. The major cations were eluted as described above; barium was eluted with 8 M nitric acid and precipitated as its sulphate.

The activity of the precipitate was measured with the scintillation counter and compared with a standard processed in the same way, except for the column separation. Recoveries were $\geq 99\%$.

For the determination of barium in sea-water, the resin was retained instead of the barium being eluted from the column. Barium ion exchange between the ammonium-form resin and a barium standard in 7.5 M nitric acid was examined. Amounts of resin ranging from 10 to 20 mg suspended in 1 ml of barium standard solutions ($5\text{--}15 \mu\text{g l}^{-1}$) resulted in recoveries of $>99\%$ (10 mg of resin) and $>90\%$ (20 mg of resin), relative to the standards with no resin added.

Determination of barium

Barium was desorbed from 15–20 mg portions of dry resin suspended in 1.5 ml of 7.5 M nitric acid within the microvials used for the furnace auto-sampler. The graphite tube was changed after ca. 200 firings, at which stage the absorbance had decreased by ca. 20%. Throughout the work, periodic recalibrations were made (every 6 firings). After 200 firings, no macroscopical degradation of the pyrolytic coating was observed; this only occurred after some 500 firings, the actual tube lifetime. The achieved temperature, as

TABLE 4

Column parameters and K_d values at two ammonium chloride concentrations

NH_4Cl (M)	i^a	ρ^b (ml g^{-1})	h^c cm	K_d (ml g^{-1})				
				Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
0.6	0.62	1.92	3.42	7.06	11.9	34.3	89.4	316
1.0	0.62	1.85	3.29	4.24	7.2	12.8	33.8	179

^aInterstitial volume fraction. ^bSpecific volume of resin. ^cHeight of resin column (13.4 mm i.d.).

measured with an optical pyrometer, did not differ by more than 5% from the selected temperature throughout the tube lifetime [4].

Standard solutions were prepared in 7.5 M nitric acid, as used for the sample desorption. A direct calibration graph and a standard addition graph for a natural sea-water sample had similar slopes, indicating that there was no matrix effect and that direct calibration with acidified aqueous standards is valid. This is in agreement with the fact that only small amounts of residual sea-water matrix elements remained on the column after elution with 0.6 M ammonium chloride ($\text{Na} \approx 0.5$, $\text{K} \approx 0.2$, $\text{Ca} \approx 0.2$, $\text{Mg} \approx 0.07 \mu\text{g ml}^{-1}$).

The resin particles were allowed to stand in the nitric acid in the sample cup for a few minutes. This was sufficient for the cation exchange to reach equilibrium. Under these conditions, the barium concentration in the final solution is no greater than in the sea water, but the sensitivity of graphite-furnace AAS is sufficient (4 pg Ba for 0.0044 absorbance) for determination at the levels obtained.

Reproducibility. Ten determinations of a single supernatant solution from a sample solution containing $8 \mu\text{g l}^{-1}$ barium produced an *RSD* < 2%. To check the entire procedure (column separation and graphite-furnace AAS), four 100-ml aliquots of filtered, aged Mediterranean sea water spiked with $10.0 \mu\text{g l}^{-1}$ barium were processed. The mean barium concentration found was $21.2 \mu\text{g kg}^{-1}$, and the *RSD* was 3.0%. For six samples collected within a 70-m depth interval, close to the sea floor in the NE Atlantic (FLUXATLANTE, Station 7, $46^\circ 22.01' \text{ N}$, $12^\circ 23.7' \text{ W}$; 3850 m), the mean concentration was $8.03 \mu\text{g kg}^{-1}$, and the *RSD* was 4.1%. Within such a small depth interval no gradients of barium are expected to occur.

Blanks. Untreated commercial Dowex 50W-X8 (200–400 mesh, H^+ -form) resin contains relatively large concentrations of barium, up to $1 \mu\text{g g}^{-1}$ of dry resin. Rinsing and conversion to the ammonium form decreases this barium blank to $0.04 \mu\text{g g}^{-1}$ of dry resin. Procedural blanks, run under the identical conditions used for the samples gave blank values of $0.05 \mu\text{g g}^{-1}$ barium. Depending on the initial barium content, this is equivalent to 10% (initial concentration, $15 \mu\text{g l}^{-1}$) to 25% (initial concentration, $5 \mu\text{g l}^{-1}$) of the sample concentration.

Application to sea-water samples from a N.E. Atlantic profile. Table 5 gives the data for dissolved barium along a vertical profile (4500 m) in the N.E.

TABLE 5

Concentration of dissolved barium along a vertical profile in the N.E. Atlantic, collected during the FLUXATLANTE campaign at Station 3, position $36^\circ 15.2' \text{ N}$, $13^\circ 45.6' \text{ W}$; 4460 m

Depth (m)	Barium ($\mu\text{g kg}^{-1}$)	Depth (m)	Barium ($\mu\text{g kg}^{-1}$)	Depth (m)	Barium ($\mu\text{g kg}^{-1}$)	Depth (m)	Barium ($\mu\text{g kg}^{-1}$)
19	5.1	310	6.5	1193	8.8	2961	10.2
41	5.0	506	7.3	1241	9.1	3443	12.0
61	5.3	761	7.5	1984	8.5	3924	12.9
113	6.3	1143	8.8	2473	10.0	4376	12.1

Atlantic sampled in April 1985, during FLUXATLANT'E. The concentration was found to increase from a minimum value in surface water ($5.1 \mu\text{g kg}^{-1}$) to $12.9 \mu\text{g kg}^{-1}$ in the deep sea. At the nearest GEOSECS station (station 115; position $28^\circ 1.5' \text{ N}$, $26^\circ 0.0' \text{ W}$) the surface and deep water concentrations are 5.3 and $10.8 \mu\text{g kg}^{-1}$, respectively [1].

Conclusions

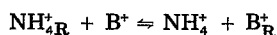
The method presented here is suitable for the routine determination of barium in sea water. The ion-exchange operation allows quantitative recovery of barium, with elimination of the major fraction of the major salt components. Barium remains on the resin, allowing for a more convenient storage of samples, as compared to its elution from the column. The subsequent batch-type desorption of barium from only milligram amounts of resin into nitric acid, just prior to the determination of barium by graphite-furnace AAS is straightforward. Further testing is required in order to decrease the barium blank values. Despite this, and the relatively complex nature of the whole procedure, barium determinations are possible with a RSD $< 5\%$ at very low levels.

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APPENDIX

Calculation of the distribution coefficient K_d for the ammonium chloride concentration range producing constant selectivity coefficients.

For monovalent/monovalent ion exchange,



The selectivity coefficient can be defined as

$$K_{\text{B},\text{NH}_4} = [X_{\text{BR}}/(1 - X_{\text{BR}})] [(1 - X_{\text{B}})/X_{\text{B}}] \quad (1)$$

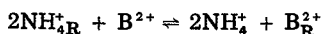
Here, X_{BR} is the equivalent fraction of B^+ on the resin, i.e., $(\text{B}^+_{\text{R}})/(\text{R})$ where (B^+_{R}) is the number of equivalents of B^+ on the resin and (R) is the total number of equivalents on the resin; X_{B} is the equivalent fraction of B^+ in solution, i.e., $(\text{B}^+)/(\text{S})$, where (B^+) is the number of equivalents of B^+ in solution and (S) the total equivalents in solution. $(\text{B}^+_{\text{R}}) + (\text{B}^+) = (\text{B}_t)$, the total equivalents of B^+ .

Equation 1 can be written as

$$(1 + K_{\text{B},\text{NH}_4}) (\text{B}^+_{\text{R}})^2 + [(B_t) - (S) - K_{\text{B},\text{NH}_4} (B_t) - K_{\text{B},\text{NH}_4} (R)] [\text{B}^+_{\text{R}}] + K_{\text{B},\text{NH}_4} (B_t) (R) = 0$$

Because K_{B,NH_4} , (B_t) , (S) and (R) are known, solution of this quadratic equation for (B^+_{R}) gives $K_d = (\text{B}^+_{\text{R}})/(\text{B}^+)$ in ml g^{-1} .

For monovalent/divalent ion exchange,



The selectivity coefficient is then

$$K_{B,NH_4} = [X_{BR}/(1 - X_{BR})^2] [(1 - X_B)^2/X_B] [(S)/(R)]$$

with all terms defined as above. This equation can be written as

$$\begin{aligned} [-1 - K_{B,NH_4}] (B_R^{2+})^3 + [2 K_{B,NH_4} - 2(S) + K_{B,NH_4} (B_t) + 2(B_t)] (B_R^{2+})^2 + \\ + [2(B_t)(S) - 2(B_t) K_{B,NH_4} (R) - K_{B,NH_4} (R)^2 - (S)^2 - (B_t)^2] (B_R^{2+}) + \\ + (B_t) (R^2) K_{B,NH_4} = 0 \end{aligned}$$

Because K_{B,NH_4} , (B_t) , (S) and (R) are known, solution of this cubic equation for (B_R^{2+}) gives $K_d = (B_R^{2+})/(B^{2+})$ in $ml\ g^{-1}$.

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