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DIRECT DETERMINATION OF DISSOLVED BARIUM IN SEA WATER BY INDUCTIVELY COUPLED PLASMA/ATOMIC EMISSION SPECTROMETRY

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SUMMARY

An inductively coupled plasma/atomic emission spectrometric technique is developed for the direct determination of dissolved barium in sea water. Matrix effects by natural sea-water components require the use of the standard addition method. The obtained reproducibility of 1.5% and the detection limit of 0.05 $\mu g\ l^{-1}$ render the technique attractive for the routine determination of barium in sea water. Results are presented for some Southern Ocean profiles and are compared with existing literature data for the same general area obtained by high-precision isotope dilution mass spectrometry.

Dissolved barium in sea water is currently measured by isotope dilution mass spectrometry [1, 2]. Considerable efforts have been made to develop other spectrometric techniques with simpler equipment. Direct methods for the determination of barium in environmental aqueous samples, including sea water, by electrothermal atomic absorption spectrometry [3–5], electrothermal atomic emission spectrometry [6–8] and d.c. plasma emission spectrometry [9] have been described. These techniques provide adequate detection limits, but are generally not suitable for routine analysis of sea water for barium owing to a lack of sufficient precision. An indirect technique, combining column separation of barium from major sea-salt components and electrothermal atomic absorption spectrometry [10] seemed more promising for the routine determination of barium in sea water.

In this paper it is shown that inductively coupled plasma/atomic emission spectrometry (ICP/AES), shown by others to be successful for the determination of trace amounts of barium in blood and urine [11], has the potential

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to yield both the detection limit and the reproducibility required for the routine determination of dissolved barium in sea water.

EXPERIMENTAL

Apparatus and operating conditions

A Jobin-Yvon JY-38 (1983 model) sequential spectrometer with a Czerny–Turner 1-m monochromator (blazed holographic grating, 3600 lines mm^{-1}; dispersion 0.28 nm mm^{-1}; resolution 0.0054 nm) is used. A demountable torch (Durr/Jobin-Yvon) is used with six turns on the load coil. The high-frequency generator (56 MHz; 5 kW maximum operating power) is free running. The sample is introduced using a concentric pneumatic quartz nebuliser (Meinhard type C). The nebuliser argon flow is previously wetted by a humidifier filled with demineralized water to avoid clogging of the nebuliser by sea-salt crystallization. The spectrometer is interfaced (two parallel DRV 11 input–output interfaces; 16 bytes) with a Digital-PDP 11/03-L computer.

The 455.40-nm line of barium was used. The operating power was generally 1.8 kW. The argon flow was set at coolant 19 l min^{-1} and sample 0.58 l min^{-1} with the nebuliser pressure set at 2.8 kg cm^{-2}. The auxiliary flow was set at 0.25 l min^{-1}. These conditions were optimized each day in order to obtain a peak-to-background ratio of at least 5 for 2.5 $\mu g\ l^{-1}$ barium solution. In the profiling mode the monochromator was set at minimal wavelength increment (0.0013 nm). The signal was integrated for 200 ms with maximal amplification.

Each determination of barium is done as follows: scanning of the 455.4-nm region (generally between 455.35 and 455.45 nm) in the profiling mode for exact location of the peak maximum and background intensity measurement (this is necessary to account for possible small drifts of the monochromator); peak-mode counting at a fixed wavelength coinciding with the maximum of the barium signal obtained in profiling mode; interpolation of the background signal at suitable distances, symmetrically about the barium peak, for obtaining the background signal at the basis of the barium peak; and subtraction of the interpolated background signal from the barium peak to obtain the net barium signal. In general, the peak-counting mode, after identification of the exact wavelength position of the emission signal maximum, yields the most reliable data.

Fifteen repeated consecutive signal acquisitions, by integration over 200 ms at the wavelength corresponding to the barium maximum, yields on average a 1% relative standard deviation (RSD).

Chemicals and sample preparation

Barium standards were prepared from commercially available standard solutions (Titrisol, Merck). Nitric acid, used for acidification of samples and standards, was of Suprapur quality (Merck). Water used for dilution of samples and standards was purified with a Milli-Q Water System (Millipore). Pure NaCl solutions (300 g l^{-1}) were prepared free from trace amounts of barium by passing them over a Diaion type CR-10 resin (Mitsubishi) with the iminodiacetate groups converted to the Na^+ form.

Sea-water samples, either filtered or unfiltered, were acidified to pH 1 immediately after sampling using nitric acid and kept at 4°C until analysis.

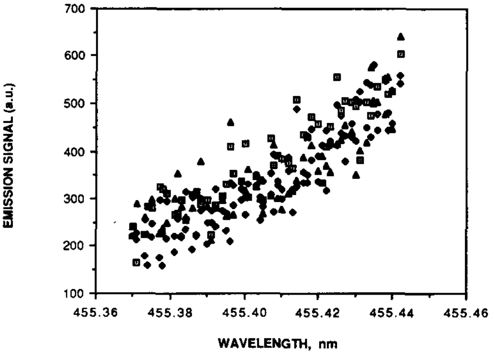
RESULTS AND DISCUSSION

Effect of increasing salt content

The production of a barium-free matrix reproducing the natural sea-water solution for matrix-effect studies is almost impossible owing to the presence of trace amounts barium in most of the chemicals required [6,9]. In this study only the possible effect of NaCl concentration on the background emission in the region of the 455.40-nm line was checked.

Solutions with different NaCl contents (25, 32, 33, 34, 35 and 40 g l^{-1}) were obtained after appropriate dilution of a barium-free 300 g l^{-1} NaCl solution with demineralized water. Figure 1 shows the emission spectra obtained in the wavelength range 455.35–455.45 nm for solutions of 0, 25, 35 and 40 g l^{-1} NaCl content. In Figure 2, the emission spectrum for 5 μg l^{-1} barium in 34 g l^{-1} NaCl solution is compared with those for 0 and 40 g l^{-1} NaCl solution without barium added. It appears that the variability of the below-peak background intensity is small and that the presence of barium has no effect on the background intensity.

For the samples with no barium added, the maximum deviation from the



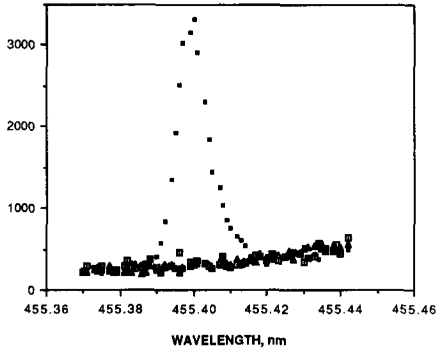


Fig. 1. Background emission signals (arbitrary units, a.u.) between 455.37 and 455.445 nm for barium-free (□) 25; (♦) 35 and (△) 40 g l^{-1} NaCl solutions and (◇) demineralized water.

Fig. 2. Emission signals (a.u.) between 455.37 and 455.445 nm for a barium-free (□) 40 g l^{-1} NaCl solution, (■) 34 g l^{-1} NaCl solution with 5 μg l^{-1} barium added and (△) demineralized water.

average background count is 11% when considering the different NaCl solutions and demineralized water together. It therefore appears that there is no systematic evolution of background emission with NaCl content.

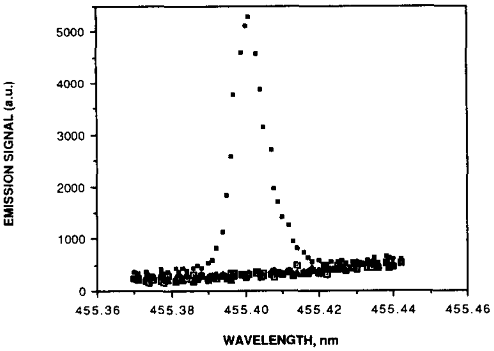
From these results, it could be tentatively concluded that the NaCl matrix and possibly the sea-salt matrix do not affect the barium signal, and therefore that the direct calibration method using standards prepared in NaCl medium could be applied. This is checked further below.

Comparison between the direct calibration and the standard addition methods

From Fig. 3, comparing the emission spectra of natural sea water (containing barium) with the 0 and 35 g l^{-1} NaCl solutions (without barium), a difference in background intensity between natural sea water and pure NaCl solution is evident. For this natural sea-water sample the interpolated background value below the barium maximum is 1.23 times the average value obtained for the different NaCl solutions and demineralized water.

It is now checked whether such a matrix effect affects the sensitivity of the method, that is, the slope of the emission signal versus concentration regression. Barium standards of 5, 10, 15 and 20 $\mu g\ l^{-1}$ were prepared in demineralized water and 34 g l^{-1} NaCl solution. The pure water and 34 g l^{-1} NaCl solution without barium added were taken as the zero. To three 5-ml fractions of a Mediterranean sea-water sample were added 1 ml of demineralized water without barium; 50 ng of barium in 1 ml of demineralized water; and 100 ng of barium in 1 ml of demineralized water, giving additions of 0, 8.33 and 16.66 $\mu g\ l^{-1}$, respectively (Fig. 4).

The relative slopes of the calibration graphs for barium in demineralized



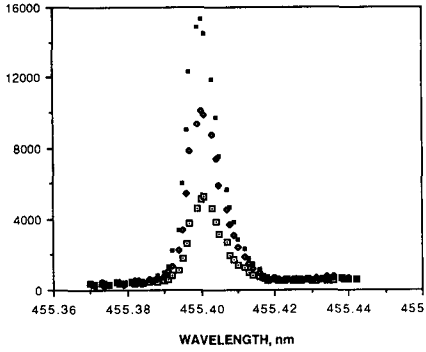


Fig. 3. Emission signals (a.u.) between 455.37 and 455.445 nm for a barium-free (□) 35 g l^{-1} NaCl solution, (△) demineralized water and (■) natural Mediterranean sea water.

Fig. 4. Emission signals (a.u.) between 455.37 and 455.445 nm for a standard addition calibration on natural Mediterranean sea water. Barium additions: (□) none; (◇) +8.33; (■) +16.66 $\mu g\ l^{-1}$.

water, 34 g l^{-1} NaCl solution and natural sea water were 100%, 99.4% and 89.4±0.04% (mean ±1 σ for five standard addition series prepared from a single sample), respectively. Whereas the slopes for demineralized water and NaCl solutions are similar, the ratio of the slope for natural sea water to that for NaCl solution is 0.9, clearly indicating that a matrix effect operates with natural sea water. Hypothesis testing (*t*-statistic [12]) indicates that the mean value of the slopes for the calibration in natural sea water is significantly different (at the 95% confidence interval) from the mean value of the pooled slopes for the calibration in demineralized water and 34 g l^{-1} NaCl solution. This observation precludes the use of the faster direct calibration method and makes the utilization of the standard addition method essential.

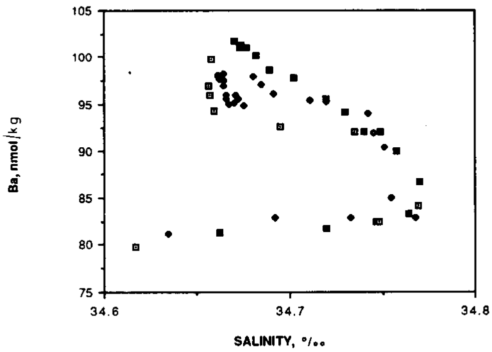
Reproducibility and detection limit

To test the reproducibility of the technique five series of samples were prepared from the same original sea-water solution, using the standard addition procedure given above. This was done for two different Mediterranean sea-water samples with different barium contents. The results obtained were 9.66 $\mu g\ l^{-1}$ (RSD = 1.7%) and 7.67 $\mu g\ l^{-1}$ (RSD = 1.2%). Hence the precision is about half that obtained by isotope dilution mass spectrometry (0.7% [1]) and is significantly better than that obtained by others using different atomic absorption and emission spectrometric techniques [6, 9, 10].

For determining the detection limit, ten below-peak background values for natural sea-water samples were calculated by interpolation of the emission signal at symmetrical distances about the barium peak. The barium concentration corresponding to the 2σ value of these background measurements was deduced from the standard addition regression on the same sea-water sample. Under these conditions a detection limit of 0.05 $\mu g\ l^{-1}$ was obtained.

Accuracy of the method

It is difficult to test the accuracy of the technique, as no reference sea water with a certified barium content is commercially available. Therefore, the present barium results can only be compared with those obtained by others for the same general area. Presented here are some Southern Ocean results obtained during the INDIGO 3 campaign (Indian Ocean sector; January–February 1987) aboard R.V. Marion Dufresne. In Fig. 5 barium–salinity plots for three vertical profiles south of the Polar Front (station I 92, 50°92′S–29°11′E, sea floor at 6435 m; station I 93, 50°41′S–29°01′E, sea floor at 4770 m; station I 94, 50°35′S–27°03′E, sea floor at 4508 m) are compared with that for GEOSECS station G429 (47°40′S–57°51′E, sea floor at 4600 m) [13]. In Fig. 6 the barium–salinity plot for Southern Ocean station I 98 (38°00′S–23°21′E; sea floor at 5325 m), located north of the Polar Front, is compared with that for GEOSECS station G93 (41°46′S–18°27′E, sea floor at 4953 m) [1]. To resolve the details for the mid- and deep water column, the plots in Figs. 5 and 6 are restricted to salinities larger then 34.6%, representing the water column from



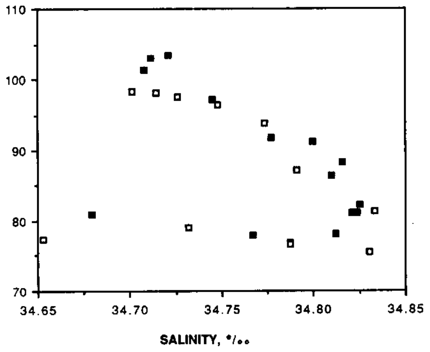


Fig. 5. Comparison of barium salinity plots between Southern Ocean INDIGO 3 stations (♦) I 92; (□) I 93 and (◇) I 94 and (■) GEOSECS station 429.

Fig. 6. Comparison of barium salinity plots between (□) Southern Ocean INDIGO 3 station I 98 and (■) GEOSECS station G93.

600–1000 m depth down to the sea floor, depending on the station. Both data sets are closely similar, with a barium range between 75 and 94 nmol kg^{-1}, a region that includes the salinity maximum of the Antarctic Circumpolar Current. With increasing depth and decreasing salinities our data indicate slightly lower barium concentrations. This feature is also apparent on the silicon–salinity plots (not shown here), suggesting that the lower barium values in the bottom waters at INDIGO 3 are genuine. A detailed description of the barium profiles will be given elsewhere.

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