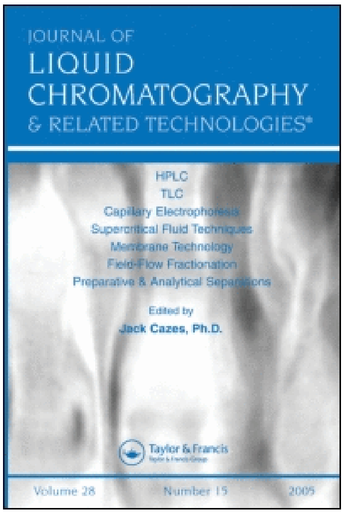

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Optimization of a Mobile Phase for Monitoring Strontium in Seawater Using Non-suppressed Ion Chromatography

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ABSTRACT

A non-suppressed ion chromatographic (IC) method has been developed for the monitoring of strontium in the presence of a large excess of alkali and alkaline earths. The mobile phase consisting of ethylenediamine (EDA) and organic acid as a complexing agent has been optimized in combination with a high-speed cationic column. The reported method has been tested, successfully, to monitor strontium in coastal Arabian seawater with a coefficient of variation 2 ($n = 5$). The reported results have been compared with ICP-OES analysis and are in agreement.

Key Words: Ion chromatography; Mobile phase optimization; High-speed column; Strontium assay in seawater.

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INTRODUCTION

Analysis of strontium (Sr) and barium (Ba) is of a great concern as regards their presence in radioactive type matrix. The strontium 90 (half life 28 years) and barium 140 (half life 12.8 days) gross activity is monitored regularly due to β-emission of these elements, and if the net activity of water sample is greater than $30\,\mathrm{pci\,L^{-1}}$, then individual concentration of these elements is monitored. Moreover, Sr concentration is also monitored in subterranean water where it is present up to several $\mathrm{mg\,L^{-1}}$.[1] However, the presence of Sr is generally accompanied by higher concentration of magnesium (Mg) and calcium (Ca). The presence of the latter two make matrix quite heavy, such as in potable and seawater. Analysis of such samples by spectrometric methods demand matrix matching of sample, standard, and blank.[2] The spectrophotometric methods for assay of Sr require masking of interfering metal ions.[3,4] Ion chromatography is well known for the analysis of ions in a variety of matrices.[5] The separation of ions with their subsequent determination minimizes the degree of interferences. Alkali and alkaline earth elements have been simultaneously separated using UV-capillary electrophoreses. However, the method lacks the capability to determine Sr in the presence of even normal Ca concentration in potable water due to close elution of analytes, and the sample dilution is pre-requisite.[6] Diffusion gradient in thin film, in combination with cationic resin embedded in poly acrylamide gel, effectively pre-concentrates Sr from solution. This method has limited application in the presence of major ions in soft water.[7] A non-suppressed ion chromatographic (IC) separation of anions and cations has been reported using eluent pyridine dicarboxylic acid alone, and in combination with 18 crown-6 ether on a TSD gel-OA Pak column. However, it did not indicate retention behavior of Sr.[8] In a method for rapid determination of Sr, IC has been integrated in an analytical system. It has efficiently separated the co-eluted Ba from the Sr, which were not separated completely by strontium specific ion-exchanger Sr SPEC$^{\mathrm{TM}}$.[9] A suppressed IC method using mobile phase ethylenediamine (EDA)–HCl + Zn ions has been reported for the Sr determination in seawater.[10]

In the present communication, a non-suppressed cationic-IC method with an optimized mobile phase has been reported for the assay of Sr in heavy matrix, such as in seawater. The optimization of mobile phase was carried out by fixing the concentration of EDA and varying citric, tartaric, and oxalic acid at respective pHs on a fast low capacity cation column. The reported method has optimized resolution factor of (1.54), analysis time of 9 min, and it is capable of monitoring Sr in seawater. The IC method efficiency has been compared with ICP-OES and results are in agreement.

EXPERIMENTAL

Reagents

Oxalic acid, EDA (Puriss), barium chloride (Puriss), magnesium nitrate hexavalent, sodium chloride of analytical grade, and strontium atomic spectroscopy standard solution (1000 ppm) were from Fluka, Switzerland. Tartaric acid, citric acid, and calcium chloride of analytical grade were purchased from Merck, Germany. All solutions were prepared in deionized water obtained using a Syborn deionizer, USA. The prepared mobile phases were filtered through 0.45 μM pore size filters, Millipore, USA. Stock solutions of 1000 ppm were prepared for each metal ion and were standardized by EDTA.[11] The collected coastal Arabian seawater samples were immediately acidified with 1 mL concentrated nitric acid.

Instrumentation

The solvent delivery system consisting of solvent organizer K-1500, pump K-1001 installed with Rheodyne injector 7725i, and a loop of 20 μL, were from Knauer, Germany. For conductivity monitoring, an Alltech detector Model 650 was used. The column used was high-speed cation (Cat.no.269-25) from Wescan, USA. For data handling, the software Eurochrom 2000 basic edition V2.05 was used. The pH of mobile phase was set using a pH meter, 530-WTW, Germany.

Applied Research Laboratories ICP-OES model 3580 with two spectrometers, fully controlled by a PDP 11/23+ computer was also used as a counter technique for Sr analysis. The technical data for the ICP spectrometers are as follows:

Spectrometer	1 m, sequential, paschen runge 1 m, simultaneous, paschen runge
Grating	1035 grooves mm^{-1}
Torch	Fassel type
Nebulizer	Meinhard type
Gas flow	
Outer	12 L min^{-1}
Intermediate	0.8 L min^{-1}
Aerosol carrier	1 L min^{-1}
Incident power	1.5 kW
Observation height	16 mm above coil

RESULTS AND DISCUSSION

Conditions for separation of the alkaline earth elements on a cation column for their subsequent determination, were optimized for non-suppressed ion chromatography by investigating the nature of mobile phase composition. It involves concentration variation of complexing agents citrate, oxalate, and tartarate in combination with EDA at the desired pH.

Influence of Nature of Complexing Agent

Three complexing agents, namely citric, oxalic, and tartaric acid were incorporated individually in the mobile phase in combination with EDA. The use of these agents has been cited so as to improve the shape of eluted peaks.[12] It is also intended to investigate the effect of these complexing agents on the resolution and sensitivity of metal ions, particularly by focusing attention on the Ca and Sr retention behavior. Improved resolution can facilitate a more reliable assay of strontium in diverse matrices, such as in light liquid radioactive waste[13] and seawater. The mobile phase consisted of oxalic acid alone at pH 3 and 6 eluted the alkaline earths as a single peak in 5 min. Whereas, EDA alone at pH 6 separated the alkaline earths in 12 min, but peak broadening and tailing was also encountered. Therefore, appropriate concentration combinations of complexing agents and EDA was investigated. The concentration of EDA was fixed as 0.5 mM and the complexing agent concentration was varied for the optimum separation of Mg, Ca, and Sr. The details of tested mobile phases, along with chromatographic data using high-speed column, is given in Table 1. The 0.5 mM citrate mobile phase pH 6 has separation factor $\alpha = 2.1$ and resolution (Rs) 1. Also, citrate mobile phase has the best signal intensity for Sr when compared with mobile phases of oxalate and tartarate. The behavior of oxalate mobile phase regarding elution of three alkaline earths is quite encouraging, and the corresponding α and Rs are 1.56 and 1.12, respectively. However, the signal intensity for Sr is reduced when compared with citrate. It might be due to the fast ion exchange kinetics of the citrate metal complex with the column exchange sites, resulting in sharp band elution. The mobile phase consisting of EDA and 0.5 mM tartaric acid has minimum signal intensity, therefore, its further studies were discontinued. The elution pattern of the alkaline earths using three mobile phases is compared in Fig. 1.

Considering the best separation of selected alkaline earths with EDA–oxalic acid, each 0.5 mM at pH 6, further investigation was carried out with this mobile phase. The lowest detection limit (LDL) and the linear regression analysis that is the intercept and slope are given in Table 2. It

Table 1. Investigated mobile phases regarding separation of alkaline earths.

Composition of mobile phase at pH 6	Elution time[a] of Sr	Δt[b]	Response (mV)	Separation factor (α)[c]	Resolution (RS)
0.5 mM EDA + 0.5 mM citric acid	8.0	1.7	26.9	2.11	1.05
0.5 mM EDA + 2.0 mM citric acid	6.6	1.4	13.3	2.03	0.76
0.5 mM EDA + 0.5 mM oxalic acid	8.9	3.1	5.4	1.6	1.12
0.5 mM EDA + 2.0 mM oxalic acid	7.1	3.4	2.1	1.93	1.41
0.5 mM EDA + 0.5 mM tartaric acid	8.5	2.1	3.4	1.32	0.9
0.5 mM EDA + 2.0 mM tartaric Acid	9.6	1.7	1.8	1.45	1.18

[a] For metals ion standard (ppm): Mg, 1; Ca, 2; Sr, 5.
[b] Time difference between Sr and Ca.
[c] For Ca and Sr.

can be seen that the summarized data is quite attractive and could be used to measure any one of the investigated metal ions in a variety of matrices, particularly at lower concentration. This was possible among other factors also, due to the active temperature controlled background conductance correction capability of the conductivity detector. The recorded background conductance variation for the standard mixture separation was ±0.2 mV over 20 min of running time.

Effect of pH

The variation of pH may have a pronounced effect on the concerned separation of calcium and strontium. Therefore, the effect of pH and the varying concentration of acid on the separation factor were also investigated. The separation factor (α) decreases as the pH is shifted towards acidic side as shown in Fig. 2. It might be due to the increased hydrogen ion concentration, which enhanced the concentration of ethylenediammonium cation $>N^+{-}C{=}C{-}N^+<$. It increases the exchange rate of metal ions on the column resin and, hence, reduces their retention. The protonation association constants α_1 and α_2 for EDA at pH 6 are 8.89 and 7.1, respectively.[14] These

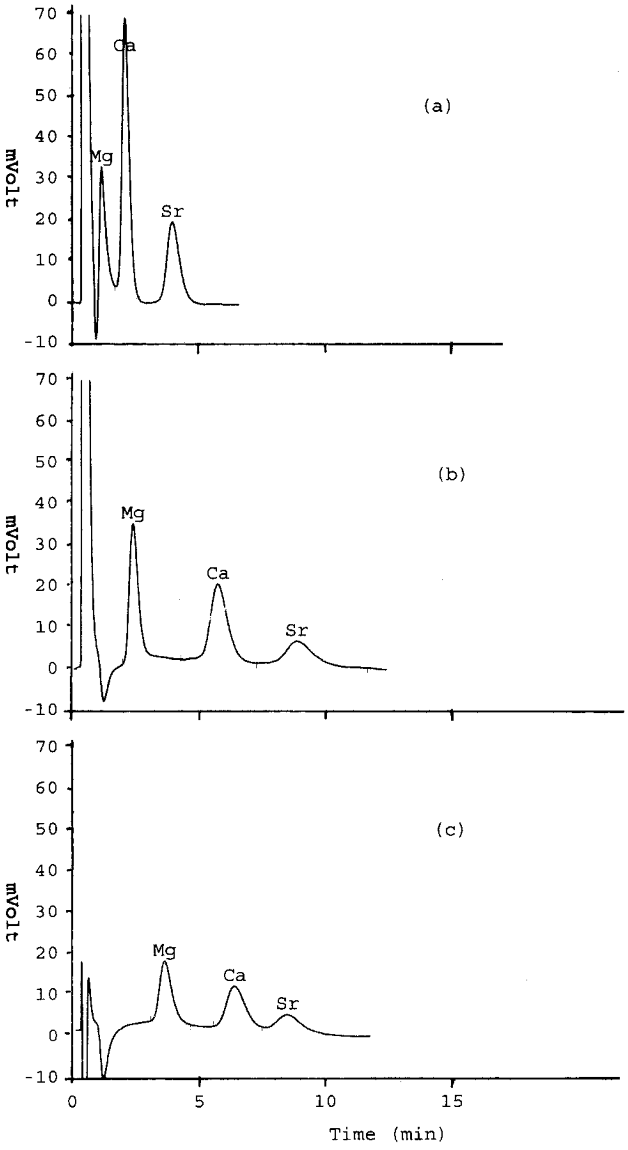

Figure 1. A comparison of elution behavior of standard metal ion mixture Mg (II): 1 ppm, Ca (II): 2 ppm, and Sr (II): 5 ppm on high-speed cationic column at flow rate $1.2\,\mathrm{mL\,min^{-1}}$, pH 6. Mobile phase: (a) 0.5 mM EDA + 0.5 mM citric acid, (b) 0.5 mM EDA + 0.5 mM oxalic acid, (c) 0.5 mM EDA + 0.5 mM tartaric acid. Conductivity F.S. = 0.1 μS.

Table 2. Linear regression analysis of chromatographic data.

Element	Lowest detection limit[a]	Slope	Intercept	Correlation coefficient
Mg	0.08	1.97 ± 0.19	7.44 ± 4.34	0.9909
Ca	0.16	0.55 ± 0.01	0.27 ± 0.36	0.9997
Sr	1.0	0.15 ± 0.01	0.25 ± 0.41	0.9966

[a] In ppm and F.S. = 0.1 μS.

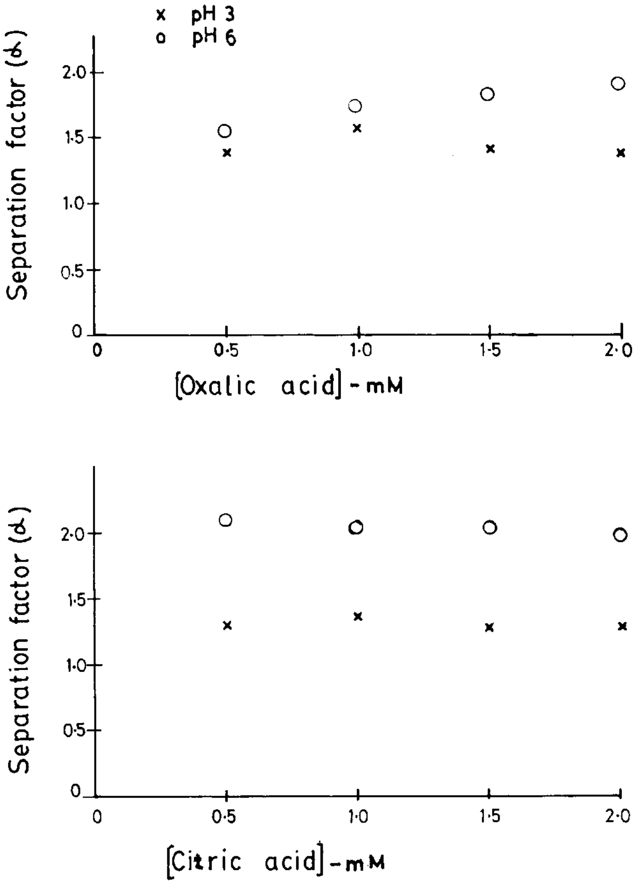

Figure 2. The variation in separation factors with the changing concentration of complexing agents, citrate and oxalate at pH 3 and 6. The rest of the experimental conditions are as per Fig. 1.

values of stability constants favor the existence of ethylenediammonium ions in the solution. The behavior of $(enH_2)^{2+}$ ion may be because of its greater affinity towards column resin due to its relatively higher hydrophobicity. The optimum pH for the present study was found to be 6.

Diverse Ion Effect

After achieving the effective separation of Ca and Sr, efforts were diverted to monitor Sr in seawater, where it is normally present in the range of 8–20 ppm.[15] However, before analyzing seawater for Sr, the efficiency of the developed IC method was tested by analyzing simulated synthetic seawater, and the results were compared with ICP-OES analysis as are summarized in Table 3. The presence of heavy matrix that is 85-fold Mg, 28-fold Ca, and 730-fold Na did not have much effect on the reported values. The elution behavior of Sr in twofold diluted synthetic seawater is depicted in Fig. 3. The replicate analysis ($n = 5$) for 10 ppm Sr showed a recovery of 73% as compared to 86% by ICP-OES. Since the concentration of Ca may affect the recovery analysis of Sr, therefore, its concentration effect on the response of Sr was also investigated as described in Fig. 4. It reveals that for optimum Sr analysis, tolerable Ca concentration is 125 ppm when Sr is around 5 ppm.

Table 3. Analysis of synthetic seawater[a] using IC and ICP-OES.

Sr concentration (ppm)			
IC			
Taken	Found[b]	CV	ICP,[c] found
3	1.6	2.9	2.97
5	3.2	2.8	4.59
8	5.1	0.36	7.54
10	7.2	2.3	8.63
13	9.1	0.60	11.07

[a] Synthetic seawater composition (ppm): Na, 11,000; Mg, 1300; Ca, 420 and dilute 1 : 2 (with double deionized water).

[b] Mean of triplicate values.

[c] RSD < 0.05%.

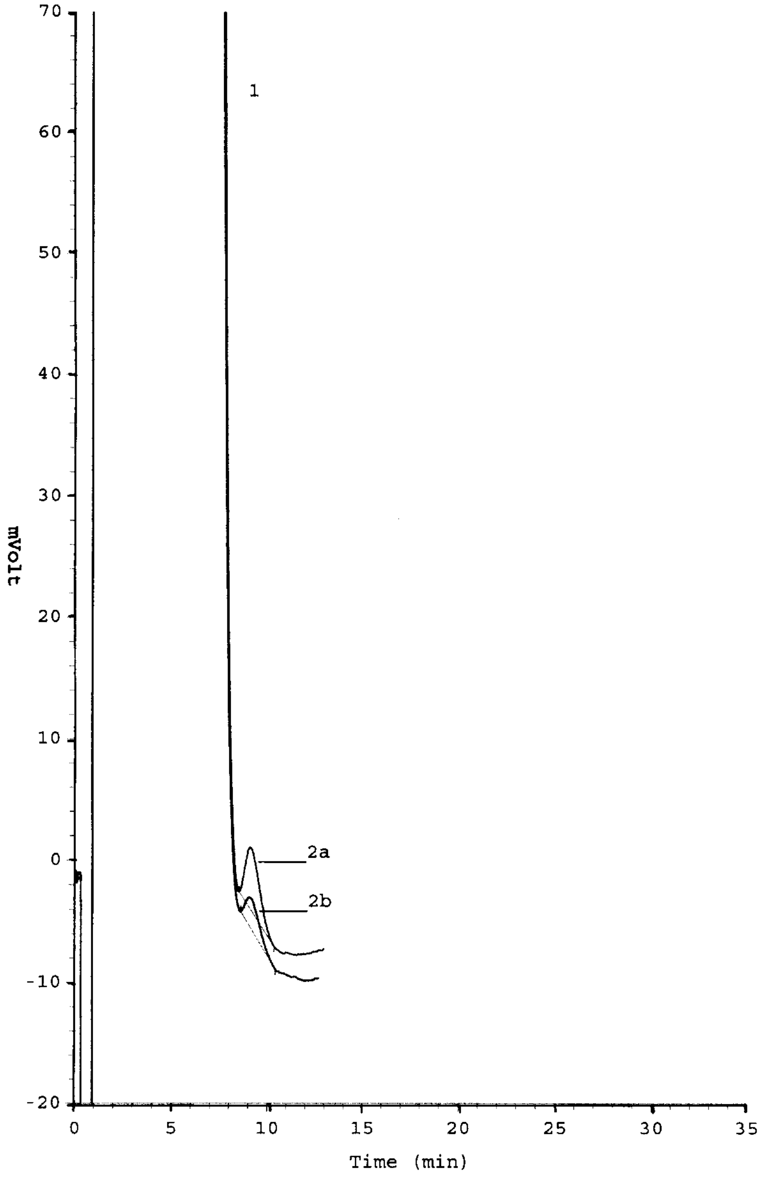

Figure 3. Monitoring of strontium(II) in synthetic seawater sample. Synthetic seawater (ppm): Na: 11,000, Mg(II): 1300, Ca(II): 420, Sr(II): 15. Mobile phase 0.5 mM EDA + 0.5 mM oxalic acid, pH 6, column: cationic, flow rate: $1.2\,\mathrm{mL\,min^{-1}}$. Conductivity F.S. = 0.1 μS. Sample diluted 1 : 2 with distilled water. Peak identification: 1, (Mg + Ca); 2, Sr (a : 5 ppm, b : 3 ppm).

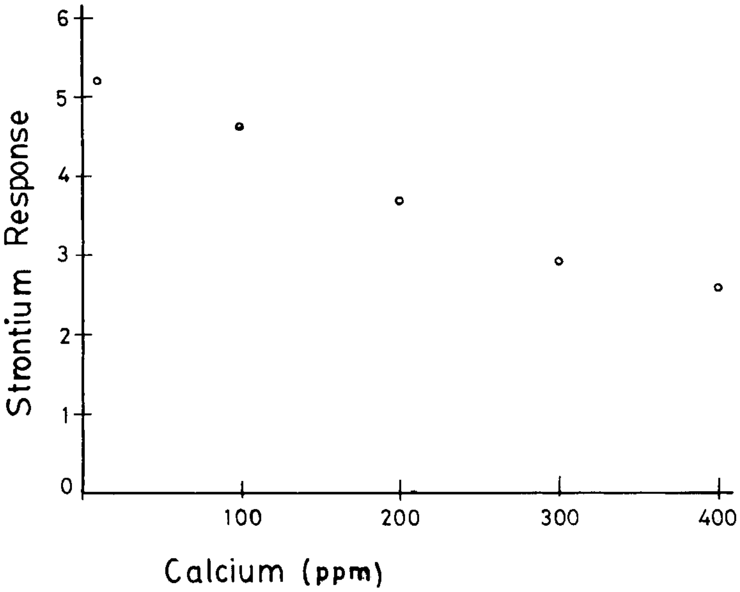

Figure 4. The effect of calcium ion concentration on the chromatographic response of 5 ppm Sr. Chromatographic conditions are as per Fig. 3.

Analysis of Sr in Seawater

It is quoted that nuclear tests are one of the possible sources of Sr 90 in the environment.[16] Therefore, a quick and simple analytical procedure, such as the present one, will be useful in monitoring the level of Sr in seawater. Moreover, a chromatographic method has the great advantage of minimum interference due to prior separation of analytes and their subsequent determination and, in particular, when using a universal conductivity detection mode. Prior to the analysis the seawater samples were passed through 0.45 μM pore size filters and were analyzed immediately. The elution behavior of Sr in these samples is shown in Fig. 5. It indicates that the reported non-suppressed IC method is capable of sensing tracer level Sr concentration changes in the samples with a heavy background matrix. Results of the analyzed samples are summarized in Table 4. It is evident from the data that the reported method has quite reasonable coefficients of variation (cv) (2%). The method was also subjected to test its efficiency using standard addition procedures. The spiked seawater samples showed a 107% recovery of the added concentration.

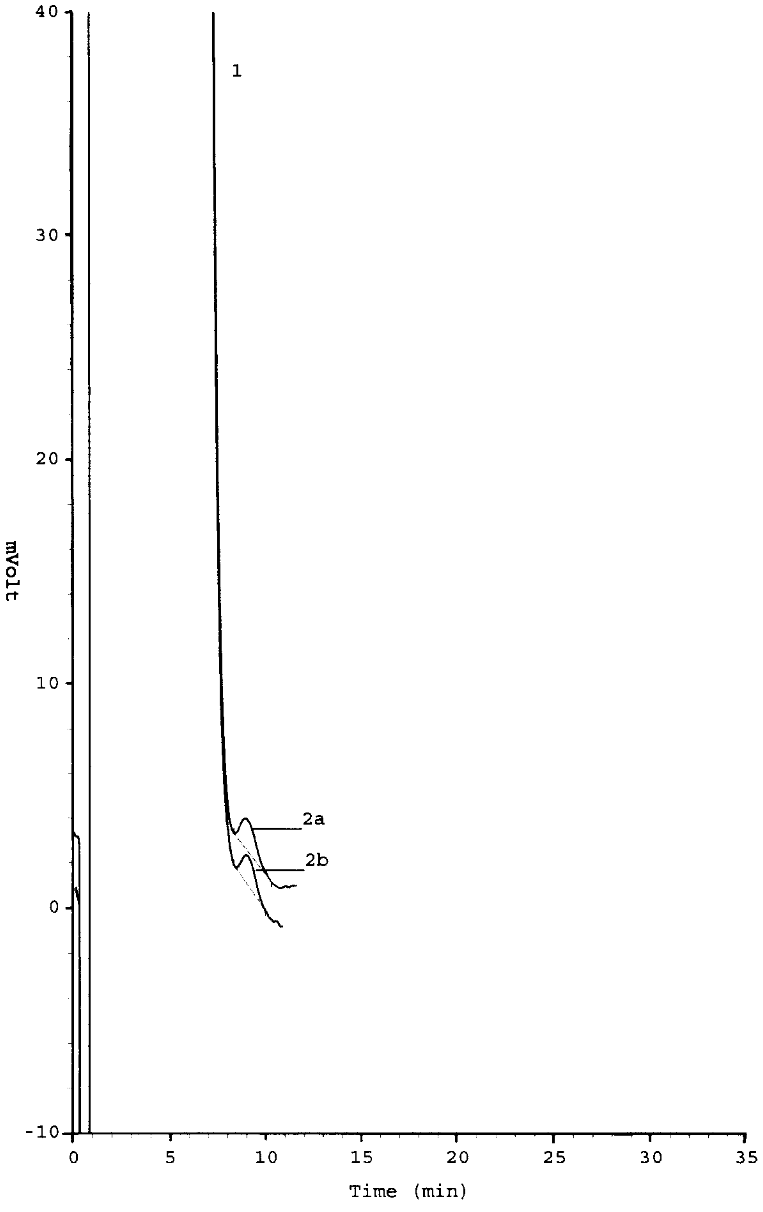

Figure 5. Analysis of strontium in seawater samples 3 and 5. Peak identification: 1, (Mg + Ca); 2, Sr (a : sample 5, b : sample 3). Samples diluted 1 : 2 with distilled water. Chromatographic conditions are as per Fig. 3.

Table 4. Monitoring of Sr (ppm) in seawater using developed IC method and ICP-OES.

Sample	IC[a]	RSD	ICP-OES[b]
1	8.0	2.09	7.62
2	6.35	2.02	7.44
3	4.7	2.5	7.5
4	6.64	1.29	6.54
5	5.23	1.86	7.0

[a] Mean of triplicate values.
[b] RSD $< 0.5\%$.

COMPARISON WITH ICP-OES

In order to evaluate the efficiency and reliability of the reported method, the seawater samples were also subjected to ICP-OES analysis. The analysis was carried out at emission line 407.77 nm with other conditions mentioned in the Experimental part. It can be seen that the ICP-OES results are in reasonably good agreement with the proposed IC method and are compared in Table 4. It enhances the reliability of the developed method.

CONCLUSION

The reported non-suppressed IC conditions are suitable for the rapid determination of Sr in the presence of large excesses of alkali and alkaline earth metals.

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