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Optimization of the procedure for the determination of alkali and alkaline-earth elements in sea water by suppressed ion chromatography

M. BETTI, G. GIOVANNONI, M. ONOR and P. PAPOFF*
Institute of Instrumental Analytical Chemistry, CNR, Department of Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa (Italy)

ABSTRACT

An ion chromatographic procedure is described for the determination of alkali and alkaline-earth metal ions in sea water the molar ratios of which, referred to lithium, are: $2.5 \cdot 10^4$ for sodium, $5 \cdot 10^2$ for potassium and calcium, and $3.5 \cdot 10^3$ for magnesium.

Lithium, potassium, magnesium and calcium are simultaneously analyzed after a 50-fold dilution, sodium is determined separately after a 2000-fold dilution. For all these elements, a dynamic range of several orders of magnitude and a R.S.D. varying from 0.2–2.2%, though typically lower than 1%, were found.

INTRODUCTION

The main aim of this research was to set up a procedure for measuring the concentrations of some alkali and alkaline-earth metal ions, namely lithium, sodium, potassium, calcium and magnesium, in sea-water samples where alkali and alkaline-earth metal ions are present at high molar concentrations: 0.5 for sodium, 0.02 for potassium and calcium, and 0.07 for magnesium (which are macro elements); $2 \cdot 10^{-5}$ for lithium (which is a microelement) [1]. The molar ratios, referred to lithium, are $2.5 \cdot 10^4$ for sodium, $5.0 \cdot 10^2$ for potassium and calcium and $3.5 \cdot 10^3$ for magnesium.

Ion-exchange chromatography was chosen for its inherent potential to obtain, under suitable experimental conditions, a good individual determination and high sensitivity for all the elements under investigation, by a restricted number of sequential chromatographic runs.

The main difficulty which had to be overcome was the vastly different selectivity of the ion-exchange resins, normally used to separate the monovalent and divalent cations, respectively [2]. These resins have a much higher selectivity for divalent cations than for monovalent cations, thus divalent cations have greater retention times than monovalent cations. Column switching, in addition to eluent-step change have been proposed to solve this problem [2,3]. In both procedures described, alkali and

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alkaline-earth metal ions are efficiently separated, provided that all the concentrations are of the same order of magnitude.

In this paper the use of eluent step-change and column-switching techniques for the simultaneous determination of lithium (at ppb[a] levels) and potassium, magnesium and calcium (at ppm levels) in the presence of high concentrations of sodium are discussed.

Because of the very large dilution required, sodium was determined in sea-water samples separately, with just a slight change in the procedure used for the other elements.

EXPERIMENTAL

Instrumentation

A Dionex Model 4500i ionic chromatograph (Dionex, Sunnyvale, CA, U.S.A.) equipped with a conductivity detector was used along with an Autolon 450 system for data acquisition and processing.

In order to minimize background conductivity and enhance the analytical response, a Dionex micro membrane suppressor (CMMS) was employed.

A cation-trap column filled with high-capacity, low-efficiency cation-exchange resin was placed between the pump and the injection valve to remove cation impurities from the eluent. The separations were carried out on CS3 and CS10 cation-exchange columns (250 mm × 4.6 mm I.D.), used in conjunction with CG3 and CG10 guard columns (50 mm × 4.6 mm I.D.), respectively.

A 50-μl loop was used for the injection of the samples. All the samples have been analyzed five times each, if not otherwise specified.

Reagents

Hydrochloric acid (Merck), 2,3-diaminopropionic monohydrochloride acid (DAP–HCl, Nova Chimica), 55% aqueous solution of tetrabutylammonium hydroxide (TBAOH, Nova Chimica) and methanol Chromosol V (Riedel de Haen) for high-performance liquid chromatography (HPLC) were supra-pure reagent-grade materials. Ultra-pure water (18 MΩ/cm resistivity at 25°C) obtained by treating double-distilled water (Carlo Erba) in a UHQ system (Elga, U.K.), was used throughout. Stock solutions (1000 mg/l) of sodium, lithium, potassium, calcium and magnesium were prepared in 0.1 *M* HCl from Tritisol (Merck) ampoules. Working standard diluted solutions were prepared daily. All standards, samples and reagents were prepared and stored in polyethylene containers, previously cleaned and conditioned following a procedure for trace element determination [4].

Eluent solution

The eluents consisted of mixtures of dilute HCl, DAP and 10% methanol, as reported in Table I, where the working conditions for the different columns are reported.

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[a] Throughout this article, the American billion (10^9) is meant.

TABLE I

WORKING CONDITIONS FOR THE DIFFERENT COLUMNS TESTED

Eluent solution composition: A = 0.25 m*M* DAP, 6 m*M* HCl, 10% methanol; B = 6 m*M* DAP, 30 m*M* HCl, 10% methanol; C = H_2O, 10% methanol; D = 100 m*M* HCl, 10% methanol.

Column	Elution program			Retention time of the last analyte, calcium (min)	Reequilibration time (min)	Total time (min)
	Time (min)	Flow-rate (ml/min)	Eluent composition			
CS3	0.0	0.5	100% A			
	10.0	1.0	100% B			
	15.0	1.5	100% C	31	15	50
CS10	0.0	2.0	5%B, 85% C, 10% D			
	7.0	2.0	50% B, 40% C, 10% D	25	20	50
CS10/CG3	0.0	2.0	5% B, 85% C, 10% D			
	4.0	2.0	5% B, 85% C, 10% D (column switching)			
	5.0	2.0	20% B, 70% C, 10% D	18	5	25

Regenerant solution for the CMMS

The CMMS was continuously regenerated with a solution of 100 m*M* TBAOH at a flow-rate of 5 ml/min. The CMMS regenerant solution was continuously recycled using a Dionex AutoRegen accessory.

RESULTS AND DISCUSSION

Optimization of the determination of lithium, potassium, magnesium and calcium

In addition to a good peak separation, two other conditions must be fulfilled in the optimization of a chromatographic procedure: firstly, all the analytes should be eluted in a moderate eluent volume; and secondly, the time for the reequilibration of the columns between runs should be as short as possible.

Different procedures were tested: (a) the use of the Ion Pac CS3 or CS10 column separately; and (b) the use of the Ion Pac CG3 column coupled with the CS10 column using the column-switching technique. The results are reported below.

Ion Pac CS3 separator. The elution of alkali and alkaline-earth metal ions on a low-capacity cation-exchange sulphonated divinylbenzene–styrene copolymer column, such as CS3, is well documented. When their concentrations are of the same order of magnitude, the use of the DAP–HCl solutions in the concentration step mode has been suggested [5]. It is reported that calcium elutes after 18 min and a further 10 min is required for column reequilibration.

With respect to lithium–sodium (and sodium–potassium) resolution, at a lithium–sodium molar ratio of 1:300, the procedure summarized in Table I has led to the best results (see Fig. 1). Methanol (10%) was added to the eluent solutions because in a preliminary investigation it was found that this organic reagent shortens both the magnesium and calcium retention times by about 5 min.

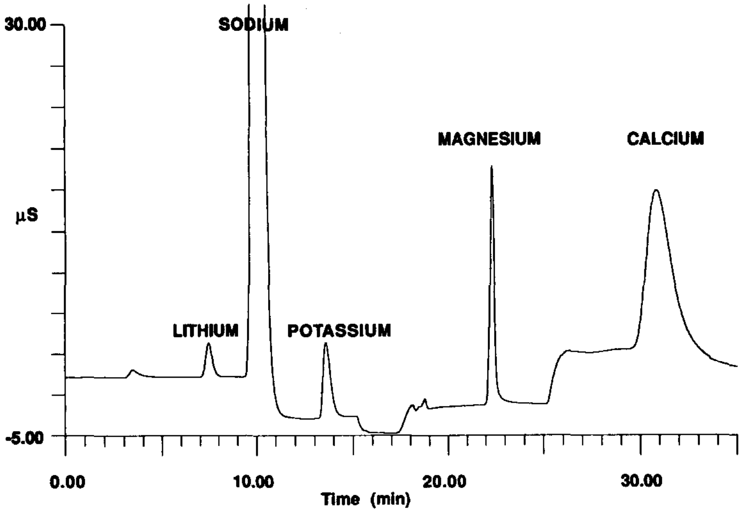

Fig. 1. Chromatogram obtained on the CS3 column by injecting 50 μl of a standard solution containing: lithium (0.5 mg/l), sodium (150 mg/l), potassium (10 mg/l), magnesium (10 mg/l) and calcium (20 mg/l). (For elution conditions see Table I.)

However, the analysis time is unacceptably long: 35 min for the analysis and 15 min for column reequilibration.

Ion Pac CS10 separator. For this column, which is also a low-capacity cation-exchange sulphonated divinylbenzene–styrene copolymer separator but with a higher efficiency than the CS3 column, it has been reported that it is possible to carry out an isocratic elution of both alkali and alkaline-earth cations, when their concentrations are of the same order of magnitude, and to separate small amounts of ammonium in the presence of a large excess of sodium as well [6].

Eluent solutions consisting of DAP and HCl mixed in different concentration ratios were tested. The chromatogram obtained by isocratic elution, with a mixture of 11.5 m*M* HCl, 0.3 m*M* DAP and 10% methanol at a flow-rate of 2 ml/min, is shown in Fig. 2. The separation between lithium and sodium is more efficient than the one obtained by the procedure described above using CS3. The so-called system peak, appearing at the void volume, is due to the high chloride concentration in this sample. In order to elute magnesium and calcium in a reasonably short time, a step to 25 m*M* HCl and 3 m*M* DAP was performed after 7 min. Even in this way, the analysis time was still unacceptably long. In fact, the ill-defined calcium peak was eluted after 25 min and the column reequilibration took 15 min. A further increase in the eluent flow-rate or the eluent concentration would sharply affect the efficiency of the suppressor column or increase the reequilibration time.

Ion Pac CG3 and CS10 —column-switching technique. Following the scheme reported in Fig. 3a, the sample, collected in the loop by a DQP pump, was injected onto the CG3 column where alkaline-earth metal cations are retained. Alkali metal ions, which are rapidly eluted from the CG3 column, are separated on the CS10 column. Four minutes after the start of the chromatographic run, the position of the

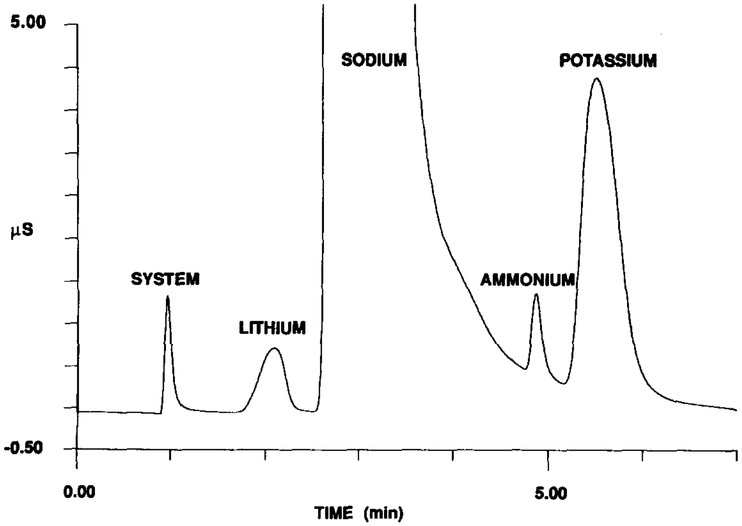

Fig. 2. Chromatogram obtained on the CS10 column by injecting 50 μl of a standard solution containing: lithium (0.1 mg/l), sodium (2000 mg/l), ammonium (8 mg/l) and potassium (2 mg/l). (For elution conditions see Table I.)

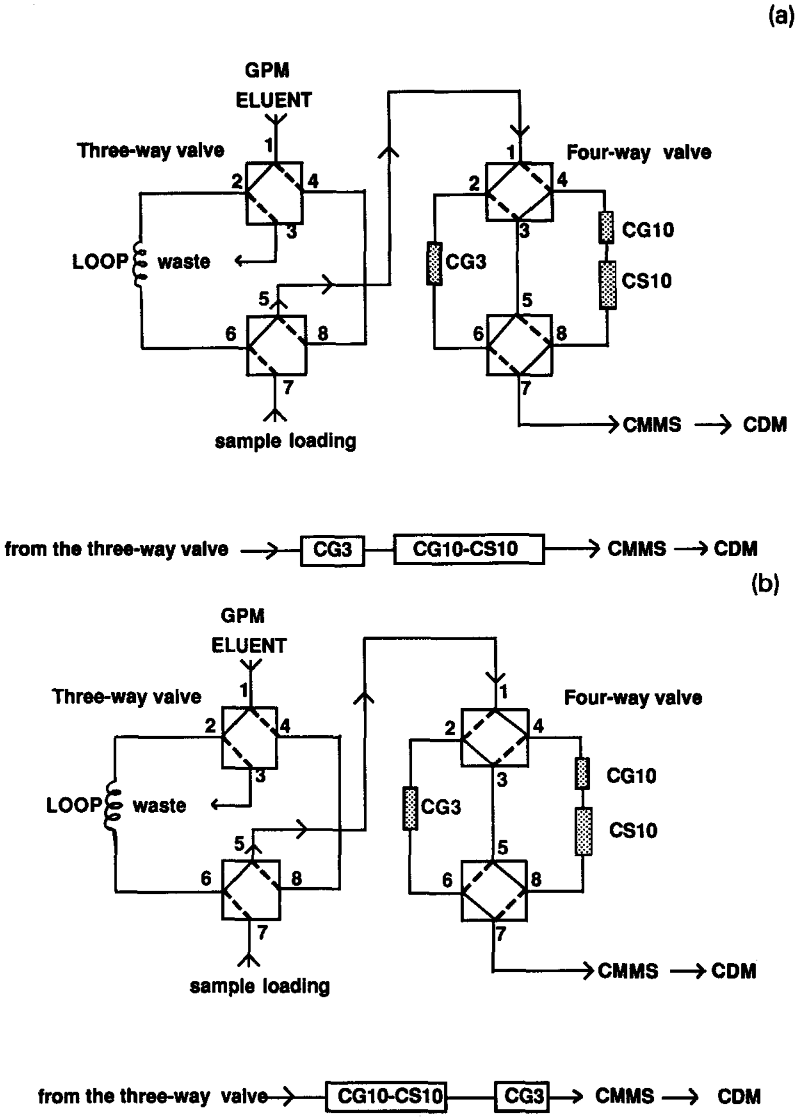

Fig. 3. Valve configuration used for the column-switching technique. The pathway of the eluent solution is represented by the solid line. (a) Before switching; (b) after switching. CDM = Conductivity detector; GPM = gradient pump.

four-way valve was changed (Fig. 3b) and the eluite from CS10 passed again onto CG3 where the separation and elution of magnesium and calcium were accomplished. In order to shorten the analysis, an eluent step was also performed after 5 min. As reported in Table I, during the first 5 min the elution was carried out with 11.5 m*M* HCl, 0.3 m*M* DAP and 10% methanol. Then the eluent was changed to 16 m*M* HCl and 1.5 m*M* DAP. Twenty minutes after the start of the chromatographic run the system was reset to the initial conditions for column reequilibration.

In Fig. 4 the chromatogram obtained for a 50-fold diluted sea-water sample is shown. The lithium peak, located at 2.46 min, refers to a concentration in the injected sample of 3 µg/l. The peaks of potassium, magnesium and calcium refer to a concentration of 6, 28 and 8 mg/l, respectively. Sodium can be measured in the same run provided that its concentration is lower than 50 mg/l.

In conclusion, by column switching coupled with the eluent step change, lithium, potassium, magnesium and calcium, in the presence of a very large excess of sodium were determined in a reasonably short time during the same chromatographic run. The calcium peak eluted at 18 min and because the change of the eluent composition was not very large, column reequilibration takes only a few minutes, leading to a total time between consecutive runs of 25 min.

Determination of sodium

When the sodium concentration in the sample is higher than 50 mg/l, as in sea-water samples, it must be analyzed separately from the other elements. In order to use the same set-up used for the other analytes with minimum modifications, the CG10–CS10 columns were eliminated and only one position for the four-way valve was used (Fig. 5). Sodium was analyzed by an isocratic elution of CG3 at a flow-rate of 2 ml/min with the eluent used in the early step of the procedure for lithium, potassium, magnesium and calcium. Thus the sodium peak eluted after 0.73 min (Fig. 6). At this dilution the other analytes are not detected as far as sea-water is concerned.

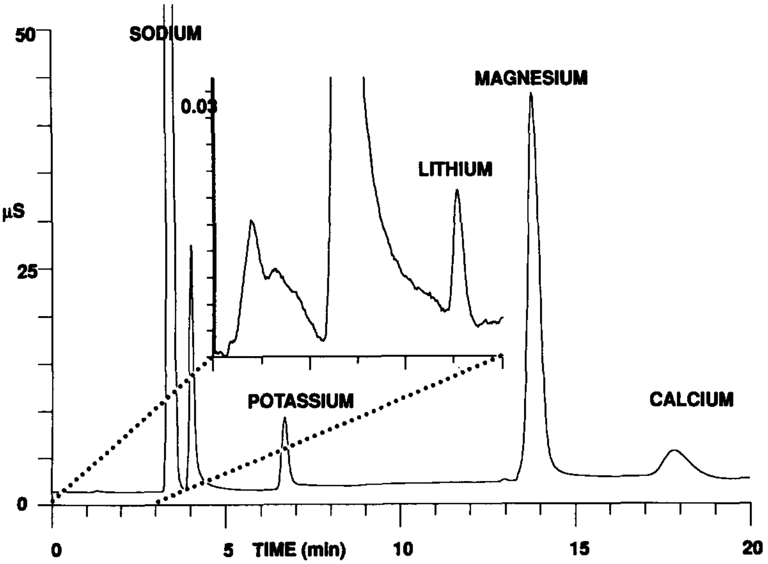

Fig. 4. Chromatogram obtained by injecting 50 µl of a 50-fold diluted sea-water sample using the column-switching technique (for elution conditions see Table I). Analyte concentrations after dilution: lithium, 3 µg/l; sodium, 200 mg/l; potassium, 6 mg/l; magnesium, 28 mg/l; and calcium, 8 mg/l.

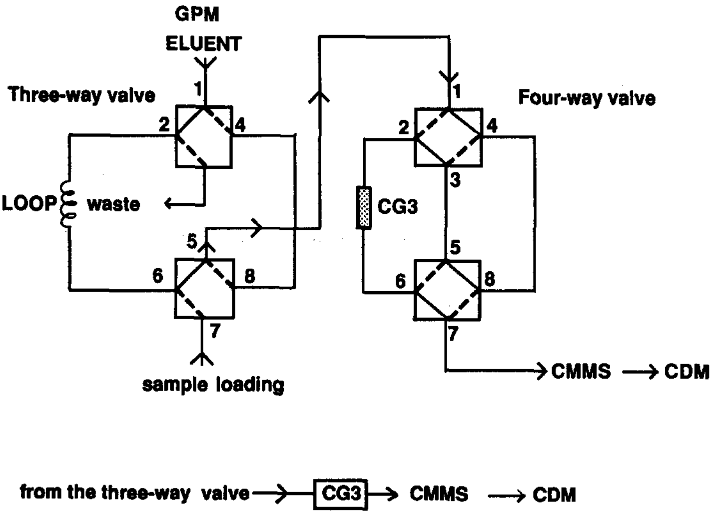

Fig. 5. Valve configuration for sodium analysis. The pathway of the eluent solution is represented by the solid line.

Range of concentrations tested, retention times, and relevant relative standard deviations (R.S.D.)

For each element the sensitivity *S*, *i.e.* the ratio of the peak area and concentration, has been found to be an unambiguous value in the range of concentration tested (several orders of magnitude). The range of these concentrations with the retention times and relevant R.S.D. values are shown in Table II. The R.S.D. was found to be

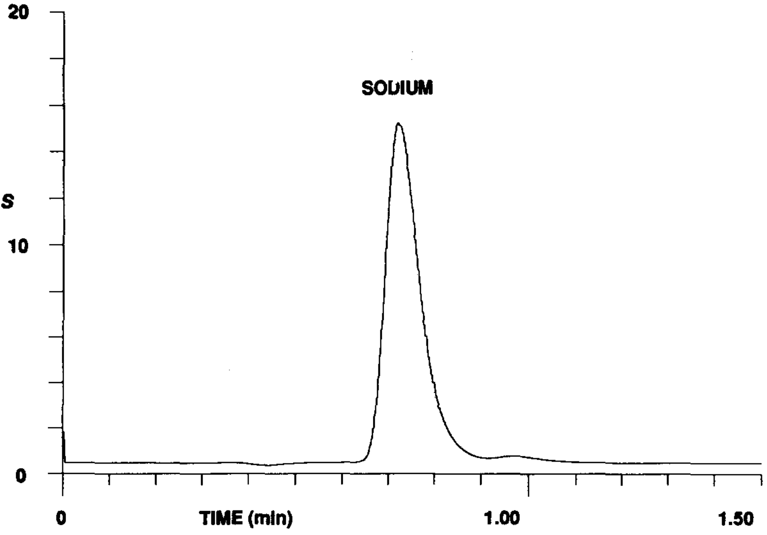

Fig. 6. Chromatogram obtained by injecting 50 μl of a 2000-fold diluted sea-water sample. Sodium concentration after dilution: 5 mg/l. Isocratic elution performed on a CG3 with 11.5 mM HCl, 0.3 mM DAP and 10% methanol.

TABLE II

RANGE OF CONCENTRATIONS TESTED, RETENTION TIMES AND RELEVANT R.S.D.

Elements	Range of concentrations tested	R.S.D.[a] (%)	Retention time (min)	R.S.D.[a] (%)
Lithium	5.0 μg/l- 10 mg/l	0.3–2.9	2.46	0.5
Sodium	0.1 mg/l–100 mg/l	0.1–0.8	0.73	0.1
Potassium	0.1 mg/l–100 mg/l	0.1–0.7	6.05	0.7
Magnesium	0.1 mg/l- 30 mg/l	0.2–1.8	13.82	0.3
Calcium	0.1 mg/l–200 mg/l	0.1–1.5	17.84	0.4

[a] R.S.D. relevant to 5 replicates for each concentration tested (10 replicates for lithium).

independent of concentration both for area and retention time. The area R.S.D. was lower than 1% for sodium and potassium, 2% for calcium and magnesium, and 3% for lithium. These differences, which can be considered effective and not casual, can be attributed to the exchange-mechanism differences of the individual ions on the suppressor membrane.

As observed for anions [7–10], calibration graphs are non-linear. In the present case the curves are precisely described by an empirical equation of the form: $Y = c + bC + aC^2$ (eqn. 1), where Y is the peak area, and C the analyte concentration. Lithium, for instance was measured systematically for eleven concentrations in the range $5 \cdot 10^{-3} - 10$ mg/l: ten replicates were performed for each sample. Depending on whether the data were on all or only on the seven highest concentrations tested, the value of c was negative and went from -0.10 to -0.84 while the relative standard error of estimate (R.S.E.), *i.e.* the R.S.D. about the regression line, goes from 1.9 to 0.9. Furthermore, when the highest concentrations values are disregarded, depending on whether the first five or the first nine lowest concentration values are considered, c, b, a, and R.S.E. remain quite stable: c ranges between -0.08–-0.09, b between 0.154–0.152, a between $4.6 \cdot 10^{-6}$ to $4.0 \cdot 10^{-6}$ and the R.S.E. between 1.4 and 1.8%.

From the above findings and by considering that even at the lowest concentrations of lithium, it has been proved that the solutions do not exchange with the container walls and are stable for months, it is possible to assess that the negative value of the intercept is not assignable to experimental effects, such as an incorrect instrumental baseline subtraction (in the integration step) nor to a loss of lithium in the chromatographic set-up at the lowest concentrations. While it is outside the scope of the present paper to ascertain the physical meaning of this behaviour, possible reasons are (a) the non-linear relationship of the conductivity of salts with concentration [11]; (b) systematic errors due to the conductivity cell design and conductivity measurements, and (c) changes in the background conductivity of the eluent, with or without the analyte, due to variations in the membrane exchange mechanisms or to a rearrangement of the equilibria in the solutions.

In Fig. 7 the contribution of the terms c, $c+bC$ and aC^2 respectively, to Y are shown *vs.* concentration, for lithium. The intercept term c is significant ($>0.5\%$) up to 200 ppb, while the quadratic term aC^2 is significant for concentrations higher than 500 ppb. These findings must be considered whenever a standard addition procedure is used. In this case systematic errors are introduced whenever S is not constant with the concentration. The size of error depends both on the original analyte concentra-

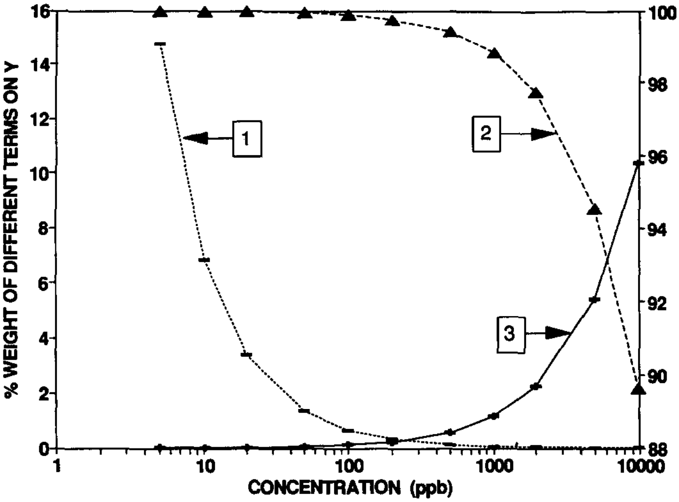

Fig. 7. Contribution of the different terms of eqn. 1 (see text) on the calculated area Y, for lithium. Curves: 1 = percentage c/Y; 2 = percentage $(c+bC)/Y$; 3 = percentage aC^2/Y. Curves 1 and 3: left scale; curve 2: right scale.

tion and on the amount of analyte added to the solution in the standard addition step. In Fig. 8 errors are shown *vs.* the apparent concentration found, as was calculated simulating for several concentrations of lithium, in the range 5–4 · 10^3 ppb, two standard additions which lead, respectively, to a double- and three-fold increase in the original concentration.

The values of the parameters in eqn. 1 and in general the values of $S(Y,C)$ for all

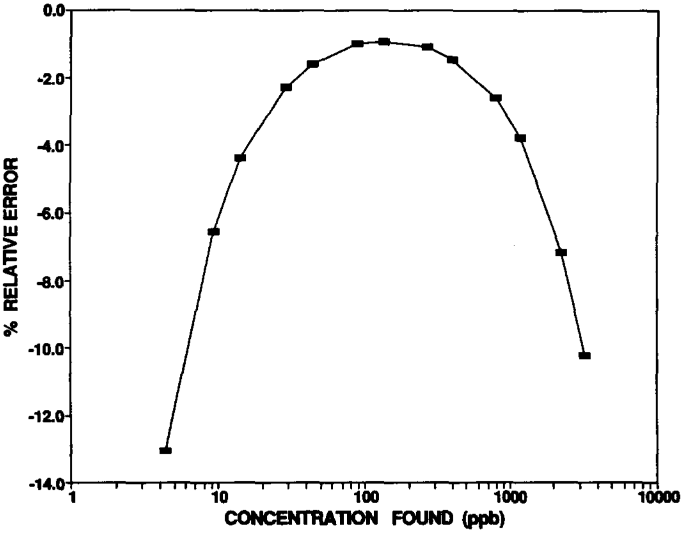

Fig. 8. Relative error *vs.* apparent concentration for lithium as calculated by simulating two points standard additions.

TABLE III

EFFECTS OF STORAGE TIME AND DIFFERENT ANALYTICAL PROCEDURES SAMPLE STATISTICS

Data refer to the 1988–1989 Italian Antarctica expedition (Ross Sea). All the mean concentration values ($\bar{x}$) are expressed in mM units with the exception of lithium whose values are in μM units. $R = \bar{x}_n/\bar{x}_1$ (n = second or third line data for each station). R.S.D. relevant to 5 replicates.

Station	Date	Element														
		Lithium			Sodium			Potassium			Magnesium			Calcium		
		$\bar{x}$	R	R.S.D. (%)	$\bar{x}$	R	R.S.D. (%)	$\bar{x}$	R	R.S.D. (%)	$\bar{x}$	R	R.S.D. (%)	$\bar{x}$	R	R.S.D. (%)
1	29.05.90	26.27		0.92	450.7		0.25	5.86		1.71	55.2		0.53	14.70		0.95
	10.01.91				455.0	0.990	0.38	5.98	1.020	1.53	55.7	1.009	0.76	15.00	1.020	1.09
	15.01.91	26.10	0.994	1.09	454.2	0.992	0.29	5.93	1.012	1.35	56.0	1.014	0.65	14.80	1.007	0.87
2	29.05.90	23.18		0.70	438.2		0.39	7.09		1.41	52.9		1.32	11.20		0.42
	11.01.91				440.0	0.996	0.46	7.06	0.996	1.09	53.3	1.008	0.97	10.80	0.964	0.65
	16.01.91	23.00	0.992	0.83	439.2	0.998	0.42	7.03	0.991	1.23	53.7	1.015	1.22	11.00	0.982	0.56
3	29.05.90	24.56		0.85	453.5		0.33	7.57		0.53	54.8		1.22	8.50		1.09
	10.01.91				450.0	0.992	0.53	7.61	1.005	0.96	54.4	0.993	1.14	8.67	1.020	0.97
	16.01.91	25.00	0.982	1.03	451.0	0.994	0.45	7.60	1.004	0.76	54.0	0.985	1.07	8.70	1.023	1.06
4	29.05.90	24.10		1.40	447.5		0.62	7.50		0.40	53.5		0.59	10.70		0.84
	11.01.91				451.0	1.008	0.57	7.43	0.991	0.65	54.0	1.009	0.63	10.50	0.980	0.56
	16.01.91	24.00	0.996	0.99	449.7	1.005	0.95	7.50	1.000	0.74	54.0	1.009	0.67	10.20	0.953	0.72
5	29.05.90	23.80		1.34	443.7		0.92	6.34		0.32	56.2		0.30	12.80		1.29
	15.01.91	24.00	1.008	1.25	444.0	1.007	0.67	6.30	0.994	0.46	56.0	0.996	0.28	13.00	1.016	1.14
6	29.05.90	23.50		1.32	441.7		1.12	7.47		0.27	57.8		0.27	13.20		1.09
	15.01.91	23.50	1.000	1.09	440.0	0.996	1.04	7.50	1.004	0.33	58.0	1.003	0.31	13.00	0.985	1.95

the elements considered, are reproducible for 1 month with an R.S.D. of 2%. Refreshing of the equation parameters can be performed by replicating the measures, say nine times, for three significant concentration values, covering the range of interest. In the case of lithium these concentrations are: 5 ppb for a good estimate of the intercept c; 100 ppb for a good estimate of b; and 4000 ppb for a good estimate of a.

Analysis of sea-water samples

All the sea-water samples were filtered through a 0.45-μm membrane filter by means of a closed system pressurized with nitrogen, acidified at about pH 2 (2 ml of 10 *M* HCl per liter) and stored at 4°C in 1-l high-density linear polyethylene containers which had previously been cleaned and conditioned [4] in our laboratory. Two 1-l containers were filled for each sampling station.

Before the injection, the samples were passed through a Dionex OnGuard-RP cartridge to remove humic substances. There was a 100% recovery concentration from this cartridge for all the analytes considered in this investigation. Lithium, potassium, magnesium and calcium were measured after a 50-fold dilution of the sea-water samples. For sodium a 2000-fold dilution was necessary.

The cumulative effect due to the storage time of the samples and to the different procedures of analysis on the scattering of the mean value $\bar{x}$, are shown in Table III. Six sampling stations, relevant to the 1988–1989 Italian expedition in the Ross Sea (Antarctica) are considered. For each station the first horizontal line refers to samples analyzed according to the first procedure used, the other two lines refer to the second procedure. The percentage variation of the ratio $\bar{x}_n/\bar{x}_1$ (n = second or third line) was higher than 1%: (i) practically every time for calcium (maximum variation: 4.7%); (ii) three times for magnesium (maximum variation: 1.5%); and (iii) once for lithium and potassium (maximum variation: 1.6 and 2.0%, respectively) and never for sodium (maximum variation: 0.8%).

Comparison of the sea-water composition between stations and between two consecutive expeditions is in progress.

CONCLUSIONS

Chemically suppressed ion-exchange chromatography, using the column switching technique coupled with an eluent step change, is very effective for the simultaneous determination of lithium at μg/l levels, potassium, magnesium and calcium at mg/l levels, and sodium up to 50 mg/l. For higher concentrations, sodium is analyzed separately in a second run after a proper dilution.

The procedure was successfully applied for the analysis of sea-water samples.

The variation within months (7 months) between mean values was lower than: 1% for sodium, 2% for lithium, potassium and magnesium, and 4% for calcium.

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