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Suppressed ion chromatographic determination of lithium, sodium, ammonium and potassium concentrations in sub-surface brines¹

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Abstract

Suppressed ion chromatographic method for simultaneous determination of lithium, sodium, ammonium and potassium in sub-surface waters of high salinity has been reported. A short column, Dionex CG-2 (50×4.6 mm I.D.), was used as separator column in combination with another CG-2 column as guard column with 0.005 mol l⁻¹ HCl as eluent at 2.0 ml min⁻¹ flow-rate. High resolution between lithium/sodium, sodium/ammonium and ammonium/potassium peaks allowed baseline separation of these cations even though the molar concentrations of lithium, and potassium and ammonium differ from sodium by about 500 and 50 times, respectively. A single calibrating solution, containing lithium at 0.035 mg l⁻¹, sodium at 54 mg l⁻¹, ammonium at 0.7 mg l⁻¹ and potassium at 2.5 mg l⁻¹ was used to determine the concentrations of these ions in water samples using a computerized routine. Total average analysis time of approximately 10 min (including column cleaning time) was considerably shorter than that reported in the literature. Due to its good reproducibility (%R.S.D.<2.5%) and accuracy (established by method comparison), the method was adopted for routine analysis of ammonium and alkali metals lithium, sodium and potassium in sub-surface waters, seawater, ground waters of high salinity and aqueous extracts of soil and aerosols.

Keywords: Water analysis; Metal cations; Inorganic cations; Suppressed ion chromatography; Sub-surface brines

1. Introduction

Ion chromatography (IC) has been accepted as a routine method of anion analysis [1–11] but has not yet been adopted as the method of choice for the determination of cations. The reason for this simply may be that ion chromatography cannot compete

with the rapidity of analysis carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Although ICP-AES will continue to be the workhorse instrument for the quantification of metal cations, IC can be developed as an supplemental technique to atomic spectroscopy as modern analytical laboratories incorporate both ICP-AES and IC, the latter normally for anion analysis. Moreover, IC can be used for the determination of special cations such as ammonium which cannot be determined by ICP-AES.

Recently, we have reported a suppressed ion chromatographic method for the determination of

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¹ This paper is dedicated to Dr. Mikio Chiba at the occasion of his retirement.

magnesium, calcium and strontium in sub-surface waters [12]. The aim of this investigation was to develop a fast, suppressed ion chromatographic method for the simultaneous determination of lithium, sodium, ammonium and potassium in high-salinity sub-surface waters.

2. Previous literature

Separation of alkali metals and ammonium ion by suppressed ion chromatography has been described in the literature [13–17]. Sodium, ammonium and potassium can be separated from each other on a Dionex CS-1 (250×4.6 mm I.D.; Dionex, Sunnyvale, CA, USA) analytical column and CG-1 (50×4.6 mm I.D.) guard column with 5–8 mmol l⁻¹ nitric or hydrochloric acid used as eluent. However, none of the previously mentioned papers has reported the analysis of alkali metal ions or ammonium in high-salinity sub-surface waters or seawater. Moreover, the analysis time to resolve these ions was quite long, ranging from 12 to 25 min as reported in the above citations.

Rapidity of IC analyses can be increased considerably by developing methods for the simultaneous determination of desired cations. Although lithium, sodium, ammonium and potassium can be analyzed simultaneously on a Dionex CS-1 analytical column and CG-1 guard column by suppressed IC, the analysis time of approximately 12 min to resolve these ions is not efficient. Using a Dionex high-capacity CS-3 (250×4.6 mm I.D.) analytical column and CG-3 (50×4.6 mm I.D.) guard column with a strong eluent (12–48 mmol l⁻¹ HCl+0.25–4

mmol l⁻¹ DAP-HCl+0.25–4 mmol l⁻¹ histidine) [18,19], the separation of alkali metals and ammonium ions can be achieved in approximately 6 min; however, the highly concentrated eluent requires a high concentration of an expensive regenerent, such as tetramethyl ammonium hydroxide, needed for dynamic suppression [20].

In this paper we report that lithium, sodium, ammonium and potassium peaks can be resolved up to the baseline in approximately 6–8 min using two Dionex CG-2 (50×4.6 mm I.D.) guard columns with 5.0 mmol l⁻¹ hydrochloric acid as eluent. The suppressed IC conditions described in this paper were successfully used for the simultaneous determination of lithium, sodium, ammonium and potassium in high-salinity sub-surface brines obtained from Saudi Arabian oil wells, as well as in the simultaneous determination of lithium, sodium and potassium in seawater and ground waters of relatively high salinity. The determination of these ions in the above-mentioned environmental waters is important in the petroleum industry in studies concerning sub-surface formation identification, collection problems, water compatibilities, corrosion, water-quality control, water flooding, exploration, and water pollution [21].

3. Experimental

3.1. Apparatus

Ion chromatographic analyses were performed on a Dionex 2120i ion chromatograph at a constant temperature of 22±1°C, under the conditions summarized in Table 1. The ion chromatograph was

Table 1
Suppressed ion chromatographic conditions

Analytical column	Dionex CG-2
Guard column	Dionex CG-2
Suppressor column	Dionex Caton Micro Membrane Suppressor
Eluent	0.005 mol dm ⁻³ HCl
Regenerant	0.05 mol dm ⁻³ tetramethyl ammonium hydroxide (TMAOH)
Flow-rate	2.0 ml min ⁻¹
Regenerant flow-rate	4–5 ml min ⁻¹
Injection volume	100 µl
Detector	Conductivity, Dionex
Detector sensitivity	Variable
Integrator	Dionex Model 4217

equipped with a conductivity detector, and chromatographic peaks were integrated on a Dionex 4217 integrator. For comparison, lithium, sodium and potassium concentrations were determined using an inductively coupled plasma atomic emission spectrophotometer from Applied Research Laboratory, Model 3580. Ammonium was determined by a polarographic procedure similar to the one reported by McLean et al. [22] using an EG&G Princeton Applied Research Polarographic Analyzer, Model 384B.

3.2. Reagents

Doubly distilled, deionized water (Nanopure II) was used to prepare all solutions. Certified atomic standards ($1000 \pm 10 \text{ mg l}^{-1}$), used for lithium, sodium, potassium and ammonium determinations, were obtained from Fisher Scientific (Pittsburgh, PA, USA). All other chemicals used were analytical reagent grade materials.

3.3. Simultaneous determination of lithium, sodium, ammonium and potassium in sub-surface Arab-D brine by suppressed IC

All analyses were carried out using two Dionex CG-2 columns placed in series with 0.005 mol l^{-1} HCl as eluent. Arab-D brine samples were diluted 1000 times with distilled water. The ion chromatograph was calibrated with a mixed standard containing lithium at 0.035 mg l^{-1} , sodium at 54 mg l^{-1} , ammonium at 0.7 mg l^{-1} and potassium at 2.5 mg l^{-1} . Detector sensitivity was set at 1 for lithium, 100 for sodium and 3 for ammonium and potassium analyses. Although calibration curves were rectilinear for all the cations in the concentration ranges mentioned above, column overloading due to the presence of bivalent cations in the water samples required that only a single calibrating standard be run. The IC was recalibrated after every fifth sample injection as shown in Table 2.

3.4. Determination of lithium, sodium and potassium in seawater

For the determination of lithium, seawater samples were diluted 50 times and the instrument, set at the detector sensitivity of 1, was calibrated with the

Table 2

Reproducibility of lithium, sodium, ammonium and potassium determination in a sub-surface oil-field water sample obtained from a Saudi Arabian oil well

Injection	Concentration (mg l^{-1})			
	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺
Std	35 (3.20)	54 294 (4.49)	704 (6.53)	2519 (7.96)
1	34 (3.21)	53 983 (4.51)	657 (6.54)	2075 (7.98)
2	34 (3.21)	54 998 (4.49)	670 (6.53)	2153 (7.94)
3	34 (3.18)	53 793 (4.46)	657 (6.48)	2097 (7.90)
4	35 (3.17)	55 497 (4.45)	676 (6.48)	2194 (7.89)
5	35 (3.14)	55 525 (4.42)	678 (6.44)	2150 (7.84)
Std	36 (3.17)	55 828 (4.44)	725 (6.45)	2670 (7.84)
Mean ^a	34.4±0.5	54 759±825	668±10	2134±48
% R.S.D.	1.5	1.5	1.5	2.3
Re-calibrated				
7	34 (3.14)	54 162 (4.40)	657 (6.40)	2146 (7.80)

Retention time in min between parentheses.

^a Mean of five injections.

mixed standard used for the Arab-D brine sample. The instrument was recalibrated after every third injection.

For the simultaneous determination of sodium and potassium, the water samples were diluted 500 times. A detector sensitivity of 100 was used for sodium and 3, for potassium. Calibration was similar to that used for Arab-D water. Recalibration was performed after five consecutive injections.

3.5. Simultaneous determination of lithium, sodium and potassium in ground water

Ion chromatographic analyses were made by injecting 25 times diluted ground water samples. The remainder of the procedure was similar to that used for Arab-D brine.

4. Results and discussion

4.1. Determination of lithium, sodium, ammonium and potassium in sub-surface Arab-D waters

Although the molar concentrations of lithium, and potassium and ammonium, present in a sub-surface water sample differed from sodium by about 500 and 50 times, respectively, simultaneous determination of these cations was possible by changing detector sensitivity. Fig. 1 shows the separation of these ions

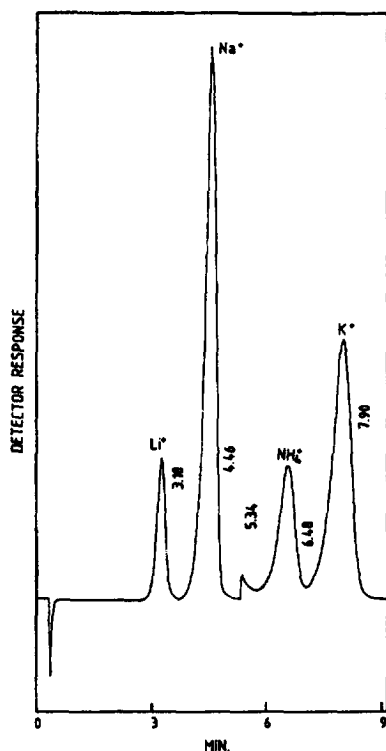


Fig. 1. Ion chromatogram showing the separation of lithium, sodium, ammonium and potassium peaks in sub-surface oil field brine obtained from a Saudi Arabian oil well. IC conditions as reported in the text.

in an Arab-D sub-surface brine sample. Table 2 shows the reproducibility of the estimation of lithium, sodium, ammonium and potassium in a subsurface water sample. On an intra-run basis maximum relative standard deviation (R.S.D.) was obtained for potassium at 2.3%. The R.S.D. value for lithium, sodium and ammonium was slightly lower at 1.5% for each ion.

The accuracy of the present IC method for the determination of lithium, sodium, ammonium and potassium in sub-surface oil field brines was assessed by comparing the IC results with those obtained by inductively coupled plasma atomic emission spectrophotometry and polarography. These results are reported in Table 3. Since only a small bias (close to 5%) was found, a good agreement existed between the two techniques.

The main difficulty in the determination of monovalent cations in sub-surface brines by suppressed IC is the irreversible adsorption of bivalent cations present in water samples. Bivalent cations do not elute with a weak eluent, such as 5 mmol l⁻¹ HCl, typically used for the separation of monovalent cations, and remain on the column. Normally, the accumulation of bivalent cations after each injection causes a slight decrease (1 to 2%, Table 2) in the retention times of the cations. Because of this, calibration routine at multilevels of analyte concentration was not successful. However, a single calibrating solution containing lithium at 0.035 mg l⁻¹, sodium at 54 mg l⁻¹, ammonium at 0.7 mg l⁻¹ and potassium at 2.5 mg l⁻¹ allowed the determination of these ions in brine samples using a computerized routine available in the Dionex Model 4217 integrator. In order to obtain reliable data for lithium, sodium, ammonium and potassium the instrument was recalibrated after every fifth injection. It can be seen in Table 2 that the variation in the results was less than 2.5% within the five injections. However, the sixth injection produced a positive error in the determination of potassium and ammonium ions. At this point, recalibration of the instrument was required in order to acquire accurate data again. The columns were cleaned using 5 to 7

Table 3

Analysis of lithium, sodium, ammonium and potassium determination in a sub-surface oil-field water sample obtained from a Saudi Arabian oil well as carried out by suppressed ion chromatography (IC) and other known methods

Cation	Concentration (mg l ⁻¹)		Bias [(X-Y)/X]·100
	Other method (X)	IC (Y)	
Li ⁺	34.0	34±0.6	0.0
Na ⁺	53 984	55 220	-2.3
K ⁺	2040	2055	-0.7
NH ₄ ⁺	720	676	6.1

Other method (X) was ICP-AES in case of lithium, sodium and potassium and polarography in case of ammonium ions analyses.

consecutive injections (similar to sample injections in a 100- μ l loop) of 3.0 mol l⁻¹ HCl saturated with EDTA when baseline resolutions between the analyte peaks was not obtained. The cleaning of the column takes 25 to 30 min without requiring any change in the flow system such as column switching or eluent change which is normally needed in case of long separator columns for the elution of bivalent cations. Typically, column cleaning was required after 15 to 20 injections and as a result total (average) analysis time per injection would increase to about 10 min (from 6 to 8 min normally required for the resolution of lithium, sodium, ammonium and potassium cations).

The problem of irreversible adsorption of bivalent cations present in water sample prompted many researchers to develop IC conditions for the simultaneous determinations of monovalent cations such as lithium, sodium, ammonium and potassium together with bivalent cations such as magnesium and calcium [18,19,23–29]. Cheam and Chau [18] reported the accuracy and precision of suppressed IC for the simultaneous determination of lithium, sodium, ammonium, potassium, magnesium and calcium ions in low ionic strength waters (such as rainwater, lakewater and riverwater) in which concentrations of determinant cations were of the same order. Considering extremely large difference in ionic strengths and molar ratios of various cations between sub-surface and river waters, the IC conditions reported in this paper cannot be extended to the analysis of sub-surface waters. The concentrations of lithium, sodium, ammonium, potassium, magnesium and calcium ions in sub-surface waters are typically reported at 35, 55 000, 700, 2100, 4500 and 30 000 mg l⁻¹, respectively. Betti et al. [30] optimized suppressed IC conditions for the separation and determination of lithium, sodium, potassium, magnesium and calcium in seawater. However, accuracy

of the determination of these ions in seawater was not established in their work.

In Table 4 we have presented calculated values of the resolution (R_s) between cation peaks eluted from various Dionex cation-exchange columns. As shown the resolution between lithium and sodium peaks was about same for all the three combinations of columns. The resolution between ammonium and potassium peaks was better for CS-3+CG-3 than obtained using the other columns. However, the resolution between sodium and ammonium ions, which may be critical in the baseline separation of a low concentration of ammonium in the presence of a large concentration of sodium, was the highest (at 2.0) for CG-2+CG-2 columns. These results suggested that long separator columns (such as the combination of a CS-3 analytical column and a CG-3 guard column, requiring a strong eluent, 12–48 mmol l⁻¹ HCl+0.25–4 mmol l⁻¹ DAP-HCl+0.25–4 mmol dm⁻³ histidine) [18,19] do not offer any advantage for the determination of monovalent cations in sub-surface waters over the use of short columns (CG-2+CG-2, requiring weaker eluent, 5.0 mmol l⁻¹ hydrochloric acid) used in the present work. In fact it is much more economic to use short columns because they cost three to four times less than long separator columns.

4.2. Determination of lithium, sodium and potassium in seawater and ground water of high salinity

The present method was also successfully applied to the determination of lithium, sodium and potassium ion concentrations in seawater and ground water of high salinity. An ion chromatogram showing the separation of trace concentration of lithium in a seawater sample is shown in Fig. 2. Baseline

Table 4
Resolution between ion pairs using different Dionex columns

Column	Resolution			Analysis time (min)	Ref.
	Li ⁺ –Na ⁺	Na ⁺ –NH ₄ ⁺	NH ₄ ⁺ –K ⁺		
CS3+CG3	1.5	1.5	2.0	6	[19,20]
CS1+CG1	1.4	1.7	1.0	12	[10]
CG2+CG2	1.4	2.0	1.3	6–8	This work

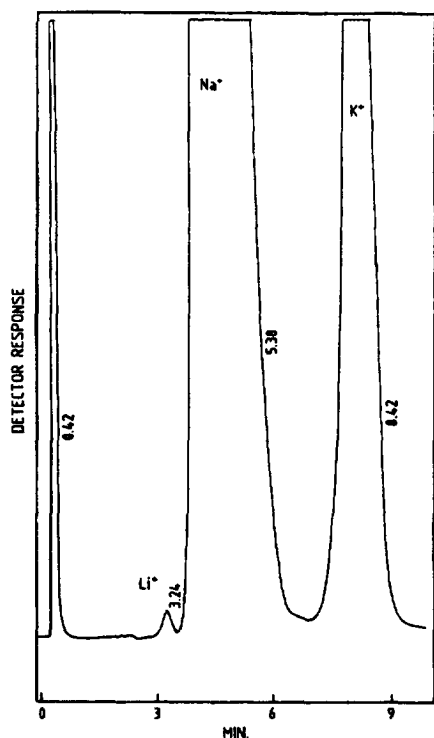


Fig. 2. Ion chromatogram showing the separation of lithium from sodium and potassium ions in a seawater sample. IC conditions as reported in the text.

resolution of sodium and potassium in seawater, and lithium, sodium and potassium in high-salinity ground water was also obtained.

Table 5 and Table 6, respectively, show the reproducibility of the estimation of sodium and potassium in seawater and lithium, sodium and potassium in ground water. On an intra-run basis, good reproducibility of the determinant cations was obtained, as %R.S.D. values ranged between 0.5 and 2.4. The reproducibility of lithium determination in seawater was also good as no variation was found in lithium concentrations, estimated from three consecutive injections. Again, the change in retention times of lithium, sodium and potassium during five injections of 500 times diluted seawater (Table 5) and 25 times diluted ground water (Table 6) was small (close to 1%).

The results presented in Table 7 revealed good accuracy of the method for the determination of

Table 5
Reproducibility of sodium and potassium determination in a seawater sample

Injection	Concentration (mg l ⁻¹)	
	Na ⁺	K ⁺
1	17 485 (4.74)	657 (8.38)
2	17 569 (4.70)	673 (8.32)
3	17 278 (4.72)	689 (8.32)
4	17 287 (4.65)	672 (8.27)
5	17 398 (4.72)	698 (8.27)
Mean	17 403 ± 126	678 ± 16
%R.S.D.	0.7	2.4

Retention time in min between parentheses.

monovalent cations in seawater, ground water and mixtures of seawater, ground water and subsurface waters.

5. Conclusion

A simple method for the simultaneous determination of lithium, sodium, ammonium and potassium in high-salinity sub-surface brines, as well as for the determination of lithium, sodium and potassium in seawater and ground waters (containing high salt concentration) is reported. The method generated sharp chromatographic peaks for all four cations which were resolved up to the baseline. This enabled accurate and reliable analysis of determinant cations in water matrices containing high salt concentrations.

Table 6
Reproducibility of lithium, sodium and potassium determination in a ground water sample obtained from a Saudi Arabian location

Injection	Concentration (mg l ⁻¹)		
	Li ⁺	Na ⁺	K ⁺
1	0.1 (3.38)	877 (4.76)	46.4 (8.38)
2	0.1 (3.37)	876 (4.73)	46.5 (8.35)
3	0.1 (3.36)	879 (4.72)	47.8 (8.32)
4	0.1 (3.37)	884 (4.72)	48.7 (8.32)
5	0.1 (3.37)	885 (4.72)	48.2 (8.30)
Mean	0.1	880 ± 4	47.5 ± 1
% R.S.D.	0	0.5	2.1

Retention time in min between parentheses.

Table 7

Analysis of lithium, sodium and potassium ions in seawater, ground water of high salinity and a mixture containing sub-surface oil field water, seawater and ground water as carried out by suppressed ion chromatography (IC) and inductively coupled plasma atomic emission spectrometry (ICP)

Water	Lithium (mg l ⁻¹)		Sodium (mg l ⁻¹)		Potassium (mg l ⁻¹)	
	IC	ICP	IC	ICP	IC	ICP
Seawater	0.26±0.008	0.26	16 650	17 790	635	630
Ground water	0.087±0.0025	0.09	892	869	44	43
Mixture	11±0.2	10.5	24 150	23 120	1068	1100

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