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Simultaneous determination of alkali, alkaline-earth metal cations and ammonium in environmental samples by gradient ion chromatography

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ABSTRACT

A gradient ion chromatographic method with chemical suppression is described for the simultaneous determination of alkali, alkaline-earth metal cations and ammonium. This fully automated ion chromatographic method was applied to determine these cations in water extracts of ambient air particulates collected on thin PTFE filters. The procedure is also potentially available for any aqueous samples.

INTRODUCTION

Since the development of ion chromatography (IC) [1], many studies [1–17] have dealt with the determination of monovalent and/or divalent cations.

Monovalent cations such as alkali metal cations and ammonium are easily eluted with dilute nitric or hydrochloric acid [2]. The separation of alkaline-earth metal cations requires the use of stronger driving ions, such as ethylenediamine [4], and are further facilitated by addition of complexing agents to the mobile phase [3,4]. The need for two eluent systems for a complete assay of mono- and divalent cations leads to double the analysis time and expenditure. To date, the simultaneous determination of alkali and alkaline-earth metal cations and ammonium by isocratic elution has been difficult.

A few methods have been reported for simultaneous analysis of alkali and alkaline-earth metal cations by non-suppressed isocratic elution with UV absorption spectrometry or conductivity detection [7–10]. Miyazaki *et al.* [7] reported a simultaneous separation of alkali metals, magnesium and calcium ions, and ammonium utilizing a silica-based cation exchanger with $CuSO_4$ solution as eluent. However, lithium, strontium and barium could not be separated. Sherman and Danielson [8] used a styrene–divinylbenzene copolymer-based cation exchanger and $Ce_2(SO_4)_3$ as an eluent for the separation of Na^+, K^+, Rb^+, Cs^+, Mg^{2+} and Ca^{2+} with indirect absorption detection. The isocratic elution of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} cations using different eluents and conductivity or UV absorption spectrometry detection had been achieved by Sato [9]. With the silica-based weak cation exchanger (Nucleosil) coated with PBDMA [poly(butadiene–maleic acid)] and a tartaric acid or a combination of citric acid and pyridine-2,6-dicarboxylic acid (PDCA) as the

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eluents, the simultaneous separation of all alkali and alkaline earth cations is reported [10,11].

Ethylenediamine, hydrochloric acid and Zn^{2+} eluent was used as an eluent on a Dionex CS2 separator column for the suppressed IC separation of Na^+, Mg^{2+}, Ca^{2+} and Sr^{2+} ions [12]. A column-switching method by using two separator columns of different dimensions and capacities, and switching them to change the flow direction during the elution was also proposed for simultaneous determination of alkali and alkaline-earth metal cations [13–16].

A new high-efficiency moderate-capacity cation-exchange column was recently introduced (IonPac CS10 from Dionex). It has been reported that it is possible to carry out an isocratic elution of both alkali and alkaline-earth metal cations [17]. However, a simultaneous determination of Li^+, Na^+, NH_4^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} with a good resolution of alkali metal cations has been a problem.

An effective way of separating ions of diverse affinities is a gradient elution technique. Gradient IC is still a new field with some problems. Suitable detection methods are difficult to find. With the advent of new high-capacity membrane suppressors, gradient elution was achieved in anion analyses [18]. Gradient elution has generally not been used in cation IC separations, mainly because many important ions can be separated and eluted isocratically. However, Cheam and Chau [19] used a step gradient suppressed IC system for separation of Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} ions.

The work presented in this study focuses on the use of a suppressed gradient IC method that allows simultaneous separation of Li^+, Na^+, NH_4^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions. This paper describes the fully automated system for the analysis of the above-mentioned ten cations in aqueous extracts of ambient air particulates and in other samples.

EXPERIMENTAL

Apparatus

A computerized ion chromatography system (Dionex 4500i, Sunnyvale, CA, USA) was used.

It consisted of an automated sampler (Dionex), a gradient pump, a micromembrane suppressor (CMMS-II), a conductivity detector (CDM-2) with autoregeneration accessory (Dionex), columns, advanced computer interface module (ACI), personal computer (IBM, PS/2 70), and a dot-module printer (Epson, FX 850).

The separations were carried out on an IonPac CS10 cation-exchange column (250 mm × 4 mm I.D.) with an IonPac CG10 guard column (50 mm × 4 mm I.D.) at a flow-rate of 1.0 ml/min. A cation trap column (CTC-1) filled with a high-capacity low-efficiency cation-exchange resin was placed between the eluent reservoir (40 mM HCl) and the pump to remove cation impurities from the eluent.

A cation micromembrane suppressor was used to minimize background conductivity and enhance the analyte conductance. The suppressor was continuously regenerated with a solution of 0.1 M tetrabutylammonium hydroxide (TBAOH) at a flow-rate of 10 ml/min. The TBAOH solution was continuously regenerated by an autoregeneration accessory. A 50-μl loop was used for injection of the samples. All samples were analyzed seven times, unless specified otherwise.

A chromatography data system (Dionex, AI-450) was used for instrument control and for data collection and processing.

Reagents

Hydrochloric acid (J.T. Baker), 2,3-diaminopropionic acid monohydrochloride (Dionex) and 100 mM aqueous solution of tetrabutylammonium hydroxide (Dionex) were of analytical reagent-grade quality.

Ultrapure water (18 MΩ/cm resistivity at 25°C) was obtained by treating the tap water in reverse osmosis and with ion-exchange columns (Millipore, RO 20 and SuperQ).

The ammonium standard solution was prepared from ammonium chloride. A stock solution of the other nine cations was prepared from National Institute of Standards and Technology (NIST) standards. Diluted working standard 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 [21].

Procedures

Standards and samples were analyzed by suppressed gradient IC under the operating conditions listed in Table I.

Multilevel calibration was used with linear least-squares best fit regression analysis. Adequacy of linear calibration of the method was tested for both peak area and peak height. Peak areas were found, in general, to have better linearities and better reproducibilities for cations.

Detection limits were calculated by analyzing dilute solutions. They were taken as three times the standard deviation of fifteen replicate analyses of a sample containing analytes with concentration equal to ten times the expected detection limit [22].

The precision of the presented analytical method was verified by replicate analysis of standard solutions containing cations of interest at $\mu g/l$ and mg/l levels. These replicate analyses were used for the determination of relative standard deviation (R.S.D.) and ensured accurate reproducibility.

Sample preparation

Filter extracts. Ambient aerosols collected on thin PTFE filters in virtual dichotomous samplers were obtained from the Pollution Measurement Division, River Road Environmental Technology Centre, Environment Canada.

TABLE I

GRADIENT PROFILE

Time (min)	Eluent 1[a] (%)	Eluent 2[b] (%)	Comments
0	100	0	Inject sample
3	100	0	Start gradient ramp
13	40	60	End gradient ramp
39	40	60	End isocratic elution
39.5	100	0	End run
55	100	0	Equilibrate and load

[a] 40 mM HCl.
[b] 40 mM HCl–20 mM 2,3-diaminopropionic acid monohydrochloride.

The samplers fractionated the aerosol into two aerodynamic size ranges yielding "fine" ($<2\ \mu m$) and "coarse" ($<10\ \mu m$) samples [20]. The samples were analyzed first by X-ray fluorescence spectrometry and then by IC.

Because the PTFE surface of the filters and some particulates are hydrophobic, it is necessary to wet the filter initially with methanol (1 ml). Particulates deposited on the filter samples were extracted using water (19 ml) by sonication for 30 min. The analysis was carried out as soon as possible after extraction.

Soil sample. A 0.25-g amount of standard reference soil sample SO-2 (Canada Centre for Mineral and Energy Technology CANMET) was acid-digested with nitric acid followed by evaporation to dryness with hydrofluoric and perchloric acids. Fluorides were displaced by heating of residue with 2.5 ml of a saturated boric acid solution and this step was repeated. The residue was then dissolved in 0.5 ml perchloric acid and 20 ml water and the solution transferred to a 100-ml volumetric flask with water.

RESULTS AND DISCUSSION

Several potential gradient elution profiles were tested to simultaneously separate Li^+, Na^+, NH_4^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. A moderate-capacity cation-exchange column (IonPac CS10) and eluent solution consisting of hydrochloric acid and diaminopropionic acid mixed in different concentration ratios were used. The procedure summarized in Table I led to the best separation of Li^+/Na^+ and Na^+/NH_4^+. All ten cations were separated with good resolution (see Fig. 1).

Analytical characteristics

The analytical characteristics of the developed procedure were determined from calibration graphs constructed for a mixed standard based on peak areas.

The linear least-squares parameters of these plots are summarized in Table II. The response is linear for all components at the concentration levels of interest.
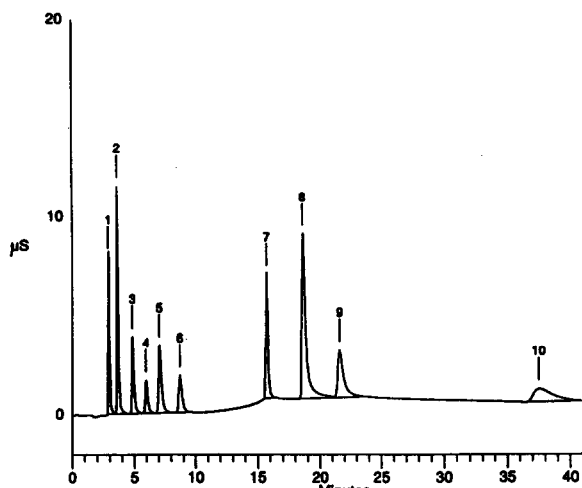
The sensitivity defined as the peak area per

Fig. 1. Simultaneous ion chromatographic separation of alkali, alkaline-earth metal cations and ammonium obtained on the CS10 column by injecting 50 μl of a standard solution. (For elution conditions see Table I). Peaks: $1 = Li^+$ (0.5 mg/l); $2 = Na^+$ (2.5 mg/l); $3 = NH_4^+$ (2.0 mg/l); $4 = K^+$ (1.0 mg/l); $5 = Rb^+$ (5.0 mg/l); $6 = Cs^+$ (5.0 mg/l); $7 = Mg^{2+}$ (1.0 mg/l); $8 = Ca^{2+}$ (5.0 mg/l); $9 = Sr^{2+}$ (5.0 mg/l); $10 = Ba^{2+}$ (10.0 mg/l).

unit concentration can be easily compared for each cation (Table II). The best response was found for lithium. The day-to-day reproducibility of the slope of each calibration curve depends on the background conductivity. Based on background conductivity values between 2 and 4 μS/cm, the relative R.S.D.s of five values of the slopes was found to be less than 6% for most of the cations under investigation. Only ammonium had a greater R.S.D. of slope (7.72%).

Blank and limit of detection

The major problem of this method are the magnesium and calcium impurities in HCl. These ions are concentrated at the front of the column when equilibrating the separator with the weak eluent (40 mM HCl). When starting the gradient, they are eluted at their expected retention times. This problem was partly solved by the use of a cation trap column in the weak eluent line. The lowest blank levels observed were 5–10 ng of magnesium and calcium.

Detection limits of analytes (for 50 μl injection volume) using described method are listed in Table II. It can be seen that most of the cations investigated are detectable in the sub-mg/l range. Lower detection limits should be possible using larger injection volumes, a concentrator column or other techniques.

Accuracy and precision

Data on the reproducibility of retention times and peak areas are listed in Table III. The R.S.D.s for the retention times of all cations are less than 0.3% and for peak areas at lower concentration level less than 4%. Ammonium was the only cation which had a R.S.D. greater than 4%. Thus, both peak areas and retention times indicate the stability and reproducibility of the system.

TABLE II

PARAMETERS OF CALIBRATION GRAPHS AND DETECTION LIMITS FOR PROPOSED METHOD

Cation	Concentration range (mg/l)	Slope (area unit/mg/l)	y-Intercept (area unit)	Correlation coefficient	Detection limit (mg/l)
Lithium	0.05– 1	$1.41 \cdot 10^8$	$-4.37 \cdot 10^5$	0.9999	0.005
Sodium	0.25– 5	$4.87 \cdot 10^7$	$3.24 \cdot 10^5$	0.9999	0.025
Ammonium	0.20– 4	$2.54 \cdot 10^7$	$2.78 \cdot 10^6$	0.9993	0.040
Potassium	0.10– 2	$2.67 \cdot 10^7$	$-2.57 \cdot 10^5$	0.9999	0.010
Rubidium	0.50–10	$1.32 \cdot 10^7$	$-7.44 \cdot 10^5$	0.9998	0.040
Cesium	0.50–10	$7.98 \cdot 10^6$	$-4.04 \cdot 10^5$	0.9999	0.050
Magnesium	0.10– 2	$7.68 \cdot 10^7$	$2.75 \cdot 10^6$	0.9997	0.050
Calcium	0.50–10	$4.67 \cdot 10^7$	$6.38 \cdot 10^6$	0.9997	0.050
Strontium	0.50–10	$2.30 \cdot 10^7$	$-1.50 \cdot 10^6$	0.9998	0.040
Barium	1.0–20	$1.14 \cdot 10^7$	$-1.24 \cdot 10^7$	0.9997	0.400

TABLE III

REPRODUCIBILITY OF RETENTION TIMES (t_R) AND PEAK AREAS

Reported results are the mean and relative standard deviation of 15 replicates for standard (STD) 1 and 5 replicates for STD 4; STD 1 (Li$^+$ 0.05; Na$^+$ 0.25; NH$_4^+$ 0.20; K$^+$, Mg^{2+} 0.10; Rb$^+$, Cs$^+$, Ca^{2+}, Sr^{2+} 0.50 and Ba^{2+} 1.00 in mg/l); STD 4 was twenty times more concentrated than STD 1.

Cation	STD 1			STD 4		
	t_R (min)	R.S.D. (%)		t_R (min)	R.S.D. (%)	
		t_R	Area		t_R	Area
Lithium	2.87	0.01	2.8	2.87	0.01	2.1
Sodium	3.67	0.21	3.2	3.65	0.21	2.1
Ammonium	4.75	0.01	5.6	4.75	0.01	4.5
Potassium	5.88	0.07	3.9	5.88	0.07	2.5
Rubidium	6.99	0.12	2.6	7.00	0.12	2.4
Cesium	8.63	0.01	3.2	8.63	0.01	2.5
Magnesium	15.65	0.05	2.9	15.65	0.05	1.5
Calcium	18.42	0.09	1.7	18.42	0.09	1.2
Strontium	21.30	0.09	2.1	21.30	0.09	1.9
Barium	37.25	0.18	3.0	37.23	0.18	2.6

In order to evaluate the quantitative performance and accuracy of the system, a certified soil SO-2 sample was analyzed. The result (see Table IV) is in good agreement with the certified values. The typical chromatogram is shown in Fig. 2.

Applications

The proposed method was applied to the simultaneous determination of alkali, alkaline-earth metal cations and ammonium in aqueous extracts of ambient air particulates collected on the thin PTFE filters and other samples.

TABLE IV

ANALYSIS OF SOIL SO-2 BY PROPOSED METHOD

Mean and 95% confidence limits for seven determinations

Cation	Found	Certified value
Sodium	2.11 ± 0.04%	1.90 ± 0.05%
Potassium	2.48 ± 0.08%	2.45 ± 0.04%
Magnesium	0.51 ± 0.01%	0.54 ± 0.03%
Calcium	1.90 ± 0.04%	1.96 ± 0.10%
Strontium	325 ± 9 μg/g	340 ± 50 μg/g
Barium	980 ± 52 μg/g	966 ± 67 μg/g

Figs. 3 and 4 show the typical chromatograms of coarse and fine filter extracts. All samples of coarse filter extracts contain sodium and calcium as major cations. Ammonium was the major cation in fine filter extracts. It is possible to detect minor peaks attributable to other alkali
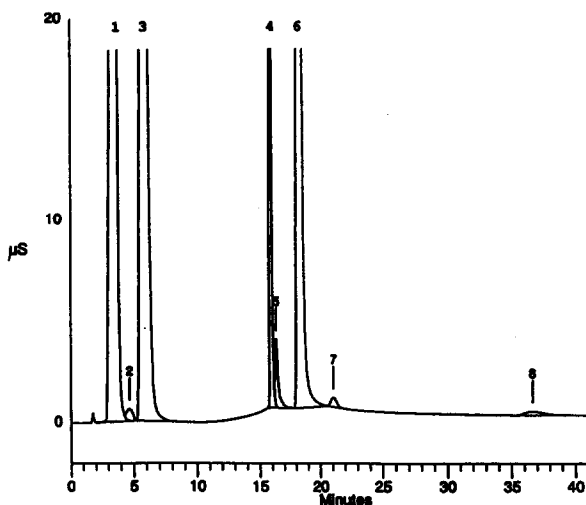

Fig. 2. Determination of alkali and alkaline-earth metal cations in a certified soil SO-2 sample. Conditions as in Table I. Peaks: 1 = Na$^+$; 2 = NH$_4^+$; 3 = K$^+$; 4 = Mg^{2+}; 5 = unidentified peak; 6 = Ca^{2+}; 7 = Sr^{2+} and 8 = Ba^{2+}.
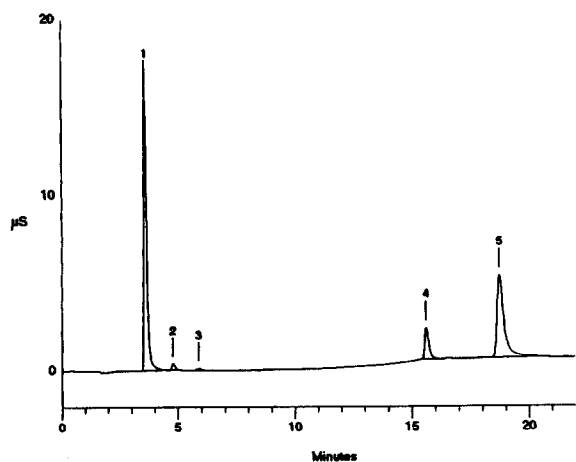
Fig. 3. Ion chromatographic analysis of a coarse air particulates extract. Conditions as in Table I. Peaks: $1 = Na^+$; $2 = NH_4^+$; $3 = K^+$; $4 = Mg^{2+}$; $5 = Ca^{2+}$.
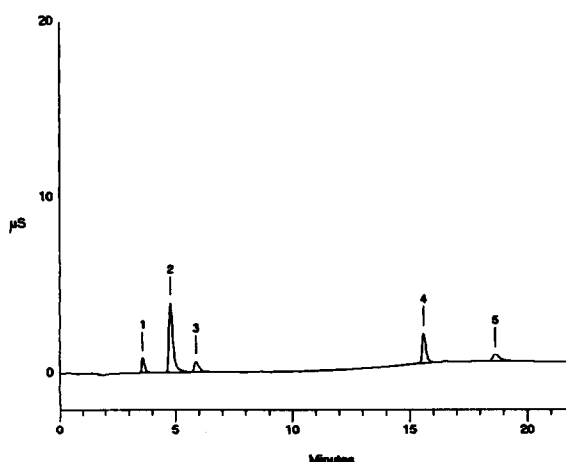

Fig. 4. Ion chromatographic analysis of a fine air particulates extract. Conditions as in Table I. Peaks: $1 = Na^+$; $2 = NH_4^+$; $3 = K^+$; $4 = Mg^{2+}$; $5 = Ca^{2+}$.

and alkaline-earth cations. The concentration of some cations such as Li^+, Rb^+, Cs^+, Sr^{2+} and Ba^{2+} is systematically or frequently under detection limit. Sometimes unidentified peaks are present. Lithium ions were found only in a few coarse filter extracts. The use of the concentrator column improves the detection limits. Strontium and barium cations were detected only in a few extract samples after preconcentration of coarse filter extracts by a factor of 100. Results of the

chemical composition (anions and cations) of the aerosols collected on PTFE filters will be reported later [23].

The proposed method was also tested to ascertain its applicability to the determination of alkali, alkaline-earth metal cations and ammonium in a tap water. The tap water sample was spiked with known amount of cation standard solutions. The recovery of all cation spikes was higher than 90% (see Table V).

TABLE V

ANALYSIS OF TAP WATER

Cation	Tap water, found ($n = 10$) (mg/l ± S.D.)	Spiked tap water		
		Added (mg/l)	Found (mg/l ± S.D.)	Recovery (%)
Lithium	0.016 ± 0.0003	0.10	0.107 ± 0.003	92.2
Sodium	7.526 ± 0.229	5.00	12.501 ± 0.381	99.8
Ammonium		1.00	0.968 ± 0.025	96.8
Potassium	1.589 ± 0.045	1.00	2.641 ± 0.063	102.0
Rubidium		1.00	0.982 ± 0.015	98.2
Cesium		1.00	0.979 ± 0.017	97.9
Magnesium	18.277 ± 0.276	2.00	20.013 ± 0.201	98.7
Calcium	39.896 ± 0.737	5.00	44.425 ± 0.664	99.0
Strontium	0.542 ± 0.014	1.00	1.408 ± 0.031	97.0
Barium		2.00	1.921 ± 0.096	96.0

Advantages and disadvantages

The main advantage of the proposed method is its applicability for multi-cation analysis of extracts of air particulates in one step. This advantage is valid for any other water sample or solution, where the volume of the sample is limited.

The disadvantage is the analysis time, which is relatively long in comparison to usually reported times for ion chromatography. This disadvantage can be compensated by overnight measurement of samples using a fully automated system.

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