

Automatic simultaneous determination of anions and cations in atmospheric aerosols by ion chromatography

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ABSTRACT

The application of an automatic quadruple ion chromatography system for the simultaneous determination of inorganic and organic anions, and inorganic cations in atmospheric aerosol extracts using a total volume of 5 ml is described. The automation of the analysis via a single loading system and analysis by anion isocratic, anion gradient (with and without preconcentration) and cation gradient methods with chemical suppression and conductometric detection is presented. Comparison of anion results obtained by the respective methods is shown.

INTRODUCTION

The measurement of the chemical, or at least elemental, composition of atmospheric aerosols is of great importance for better understanding of the nature of air pollution. Energy dispersive X-ray fluorescence spectroscopy (EDXRF) is a recognized method for analysis of elements in atmospheric aerosols collected on thin PTFE filters with virtual dichotomous samplers [1-3]. Ion chromatography (IC) is used to characterize the chemical form of compounds [2-4], because EDXRF measures only elemental composition.

IC has become the standard method of analysis for inorganic anions in many types of environmental samples. Common examples include river water, precipitation and atmospheric aerosols [5]. The value of IC for the analysis of atmospheric aerosols was first demonstrated by Mulik *et al.* [6] and was discussed in several papers presented at the 2nd Symposium on Ion Chromatography [7]. IC coupled with a concentration step is a powerful technique for trace and ultra-trace analysis [8].

Simultaneous analysis of inorganic and organic

anions and cations is of particular interest to an environmental analytical laboratory, because this approach is potentially more effective than the existing methods, where the samples are analyzed separately.

Several different chromatographic strategies have been used for the simultaneous separation of anions and cations. One of these procedures converts the cations into anions by using suitable complexing agents and then separates and detects all species as anions [9]. In another approach a mixed bed ion-exchange column containing both cation- and anion-exchanger particles was used for simultaneous separation of inorganic mono- and di-valent anions and cations using a single sample injection [10]. Dual anion and cation columns with a single conductometric detection with synchronal sample injection [11] and anion and cation columns connected in series with indirect UV detection [12,13] have been used. A general method developed by Jones *et al.* [14-17] uses a serial placement of cation and anion columns followed by conductometric detection to effect separation and measurement. Cheam and Chau [18] determined major inorganic anions and cations using a double IC system. However, none of the procedures can analyze inorganic and organic anions and inorganic cations simultaneously.

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The object of the research reported here was to develop a procedure whereby it would be possible to perform the routine separation and detection of inorganic and organic anions, and inorganic cations in a simultaneous system. Such system greatly increases the reliability and overall efficiency of the ion chromatographic procedures. This study describes the fully automated system for the simultaneous analysis of ten inorganic and organic anions and ten cations by IC in the aqueous extracts of atmospheric aerosols. The automation of the analysis via a single loading system and analysis by anion isocratic, anion gradient (with and without preconcentration) and cation gradient methods is presented. Comparison of anion results obtained by the three methods was performed.

EXPERIMENTAL

Chromatographic system

All IC equipment, columns and software used in this study were from one manufacturer (Dionex). Two personal computers (IBM, Model PS2/70) contained the operating and processing software (Model AutoIon 450). They were connected through interface modules (Model ACI). Two computerized advanced chromatography modules (Model CHA-6) were used for all anions and cations analyses. The system contained three ion chromatographs (Model 4500i) with gradient pumps (Model GPM), an ion chromatograph (Model 2110i) with an isocratic pump (Model APM), an automated sample changer (Model ASM), four micromembrane chemical suppressors (Models AMMS-II and CMMS-II), four micro conductivity detectors (Model CDM-2), four autoregeneration accessories (Model AutoRegen), four guard columns and four analytical columns.

The flow scheme of the single sample loading and injection configuration for analysis of inorganic and organic anions and inorganic cations is shown in Fig. 1. The first loading valve (V1) was connected to the anion gradient GB and cation gradient CAT channels (loading valves V2 and V3); the waste line of V3 valve was connected to valve V4 (anion gradient GA channel) and finally to valve V5 (anion isocratic IA channel) with the smallest possible dead volume between all valves.

Separation of anions and cations was carried out

on the columns and under conditions listed in Table I.

Two anion trap columns (ATC-1) were used to minimize background contamination in each anion gradient system. One cation trap column (CTC-1) was installed in the cation system in a weak eluent line.

Anion and cation suppressors were continuously regenerated with 25 mM sulfuric acid and 100 mM tetrabutylammonium hydroxide (TBAOH), respectively. All regeneration solutions were continuously regenerated by autoregeneration accessories. The chromatograms and the results were printed on two printers (Epson, Model FX-850).

Operational procedure. The quadruple IC system is simultaneously loaded and samples are injected onto the separation columns at the same time. The speed of the system is determined by the speed of the slowest method (cation gradient method). The system can operate unattended for 48 h. Stability of aqueous extracts of atmospheric aerosols is the limiting time factor. At the present time, a 24-h period of unattended operation is used.

The pumps and the valves are under computer control, as indicated in Fig. 1. Loading–injection processes are automatically achieved in a timed sequence. By monitoring the programmable controller unit (1), the valve V1 is switched to bring analyzed samples from autosampler vials into the sample loops (valves V3–V5). Next, the valve V1 is switched to load concentrator column (valve V2) with the residue of the sample (2 ml). After the sample has been loaded onto the concentrator column, it is backflushed with eluent onto the guard and the analytical columns. At the same time, the analyte from sample loops is injected onto columns for separation.

Methods

Aqueous extracts of atmospheric aerosols collected on thin PTFE filters were analyzed for inorganic and organic anions, and inorganic cations. Four methods were applied:

Anion isocratic method (IA). The separation of inorganic anions (chloride, nitrite, bromide, nitrate, phosphate and sulphate) and oxalate was carried out isocratically on an IonPac-AS4A column with an IonPac-AG4A guard column. An eluent consisting of 1.7 mM NaHCO₃ and 1.8 mM Na₂CO₃ at

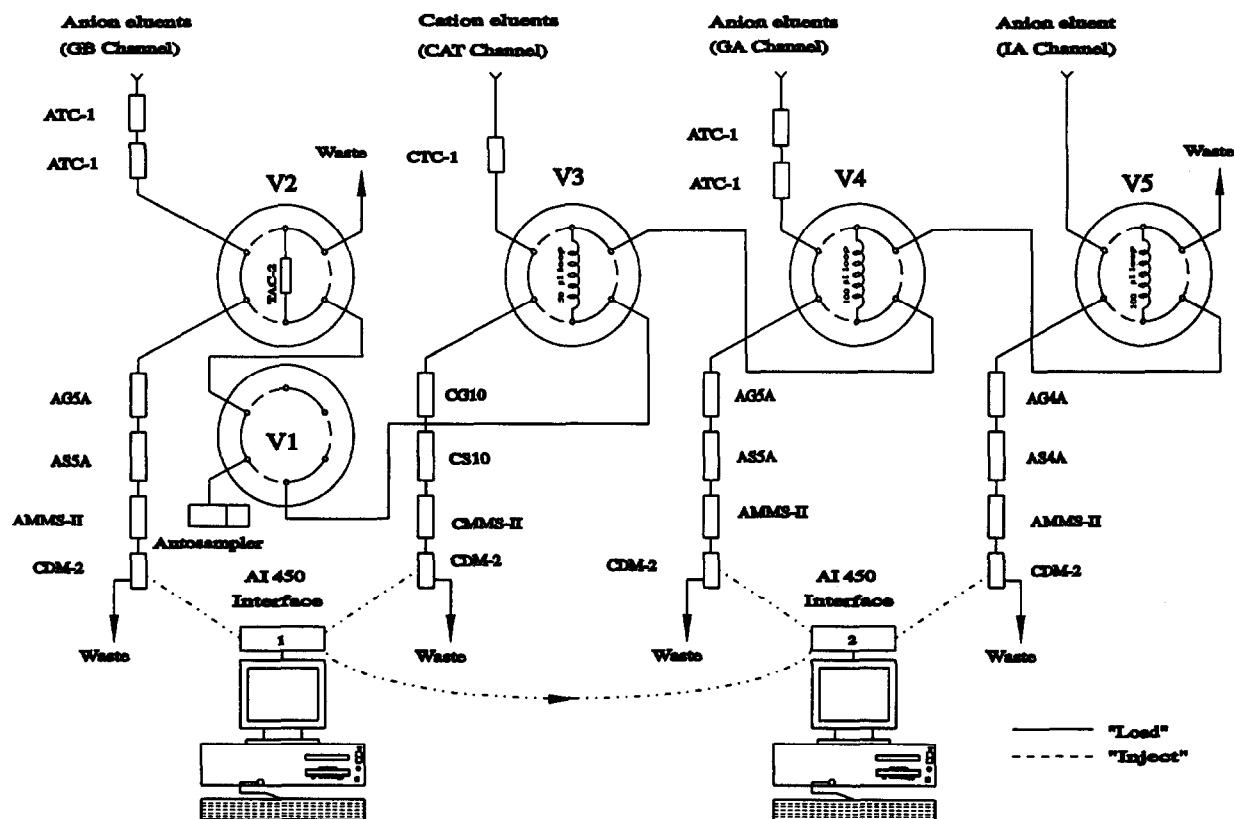


Fig. 1. The flow diagram of the single sample loading and injection configuration for simultaneous determination of anions and cations by ion chromatography.

TABLE I
EXPERIMENTAL CONDITIONS FOR ION CHROMATOGRAPHIC ANALYSIS

Parameter	IA method	GA/GB method	CAT method
Ions determined	Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , oxalate	F^- , acetate, formate, Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , oxalate	Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}
Separation column	IonPac-AS4A (250 × 4 mm I.D.)	IonPac-AS5A (250 × 4 mm I.D.)	IonPac-CS10 (250 × 4 mm I.D.)
Guard column	IonPac-AG4A (50 × 4 mm I.D.)	IonPac-AG5A (50 × 4 mm I.D.)	IonPac-CG10 (50 × 4 mm I.D.)
Micromembrane suppressor	AMMS-II	AMMS-II	CMMS-II
Eluent	1.7 mM NaHCO_3^- 1.8 mM Na_2CO_3 25 mM H_2SO_4	$E_1 = 0.75 \text{ mM NaOH}$ $E_2 = 200 \text{ mM NaOH}$ 25 mM H_2SO_4	$E_1 = 40 \text{ mM HCl}$ $E_2 = 40 \text{ mM HCl} - 20 \text{ mM DAP}^a$ 100 mM TBAOH ^b
Regenerant			
Eluent flow-rate	2.0 ml/min	1.0 ml/min	1.0 ml/min
Regenerant flow-rate	10 ml/min	10 ml/min	10 ml/min
Sample loop	100 μl	100 $\mu\text{l}/2 \text{ ml}$	50 μl

^a Diaminopropionic acid.

^b Tetrabutylammonium hydroxide.

flow-rate 2.0 ml/min was used for separation of these anions. The ions are separated in approximately 11 min. Fluoride, acetate and formate are eluting in the water dip. A chromatogram of a standard solution of these anions is presented in Fig. 2a. Other operating conditions are given in Table I.

Anion gradient method (GA). The former method gives a good separation of inorganic anions but it does not separate fluoride and some organic anions such as acetate and formate. At present, organic

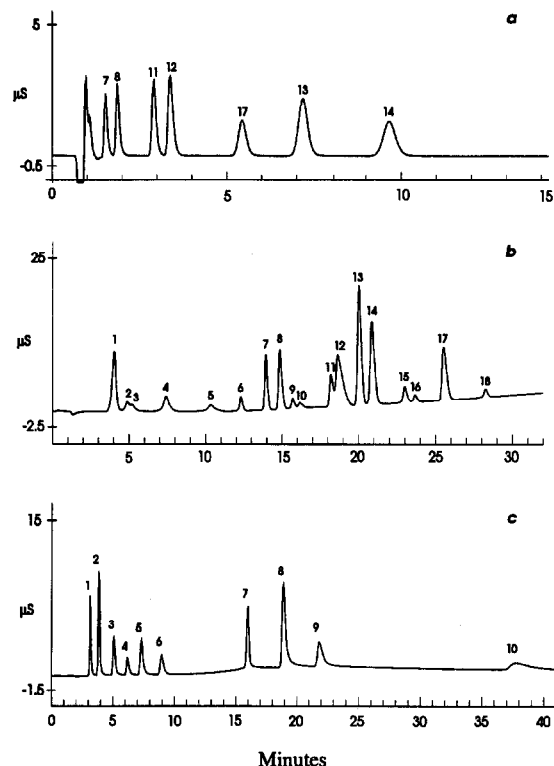


Fig. 2. Typical chromatograms of standard solutions obtained by (a) anion isotocratic IA (b) anion gradient GB and (c) cation gradient CAT methods. Peaks (a): 7 = Cl^- , 0.50 $\mu\text{g/ml}$; 8 = NO_2^- , 1.0 $\mu\text{g/ml}$; 11 = Br^- , 2.0 $\mu\text{g/ml}$; 12 = NO_3^- , 2.0 $\mu\text{g/ml}$; 13 = SO_4^{2-} , 2.0 $\mu\text{g/ml}$; 14 = oxalate, 2.0 $\mu\text{g/ml}$ and 17 = PO_4^{3-} , 2.5 $\mu\text{g/ml}$. (b): 1 = F^- , 0.05 $\mu\text{g/ml}$; 2 = acetate, 0.05 $\mu\text{g/ml}$; 3 = propionate, 0.05 $\mu\text{g/ml}$; 4 = formate, 0.05 $\mu\text{g/ml}$; 5 = methanesulfonate, 0.05 $\mu\text{g/ml}$; 6 = chloroacetate, 0.05 $\mu\text{g/ml}$; 7 = Cl^- , 0.05 $\mu\text{g/ml}$; 8 = NO_2^- , 0.10 $\mu\text{g/ml}$; 9 = dichloroacetate, 0.05 $\mu\text{g/ml}$; 10 = benzoate, 0.05 $\mu\text{g/ml}$; 11 = Br^- , 0.20 $\mu\text{g/ml}$; 12 = NO_3^- , 0.20 $\mu\text{g/ml}$; 13 = SO_4^{2-} , 0.20 $\mu\text{g/ml}$; 14 = oxalate, 0.20 $\mu\text{g/ml}$; 15 = fumarate, 0.05 $\mu\text{g/ml}$; 16 = phthalate, 0.05 $\mu\text{g/ml}$; 17 = PO_4^{3-} , 0.25 $\mu\text{g/ml}$ and 18 = citrate, 0.05 $\mu\text{g/ml}$. (c): 1 = Li^+ , 0.50 $\mu\text{g/ml}$; 2 = Na^+ , 2.5 $\mu\text{g/ml}$; 3 = NH_4^+ , 2.0 $\mu\text{g/ml}$; 4 = K^+ , 1.0 $\mu\text{g/ml}$; 5 = Rb^+ , 5.0 $\mu\text{g/ml}$; 6 = Cs^+ , 5.0 $\mu\text{g/ml}$; 7 = Mg^{2+} , 1.0 $\mu\text{g/ml}$; 8 Ca^{2+} , 5.0 $\mu\text{g/ml}$; 9 = Sr^{2+} , 5.0 $\mu\text{g/ml}$ and 10 = Ba^{2+} , 10.0 $\mu\text{g/ml}$.

compounds are arousing increased interest. Formic and acetic acids have been found to be the most abundant atmospheric organic acids [19].

Separation of major organic and inorganic anions (fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, sulphate, oxalate and phosphate) was performed on an IonPac-AS5A column with an IonPac-AG5A guard column at flow-rate of 1.0 ml/min. Gradient elution is accomplished by changing from a weak eluent (0.75 mM NaOH) to a strong eluent (200 mM NaOH) during the run using gradient program described by Rocklin *et al.* [20]. Operating conditions are presented in Table I.

Anion gradient method with concentrator column (GB). To increase sensitivity of analysis of inorganic and organic anions, the anion trace concentrator column (Model TAC-2) was used. Anions contained in aqueous extracts of atmospheric particulates are trapped on the concentrator column and are then eluted onto a guard (Model IonPac-AG5A) and analytical (Model IonPac-AS5A) columns for separation. Only 2.0 ml of analyte extract due to limited volume of the autosampler vials (5 ml Polyvial) were available for concentrator loading. Conditions for separation of anions were the same as for the anion gradient method without preconcentration. A typical chromatogram of standard mixture of anions is shown in Fig. 2b. Operating conditions are given in Table I.

As expected, no problem was observed with separation of samples of low ionic strength. However, most fine atmospheric aerosol extracts contained sulphate at high level, which interfered in the determination of nitrate, oxalate and other anions. On column elimination of high level of sulphate will be the subject of future research project.

Cation gradient (CAT) method. Ammonium and, alkali and alkaline-earth metal cations were separated on an analytical column (Model IonPac-CS10) with a guard column (Model IonPac-CG10) under conditions described previously [4]. This method is the slowest method in the quadruple IC system. The analysis time and the equilibration of the column are about 55 min. Operating conditions are presented in Table I. A chromatogram of standard solution of these cations is shown in Fig. 2c.

Quantitation procedure

Identification of individual ions is based on the

comparison of elution times of analytes with those of standard solutions.

Four standard calibrations were used with linear least-squares regression analysis. Calibrations were performed over the range of concentrations expected in the samples. Peak areas in gradient elution were found to have better linearity and better reproducibility for most anions and cations. Peak heights were used in isocratic elution.

Detection limits were calculated by analyzing dilute solutions. They were taken as three times the standard deviation of twenty replicate analyses of samples containing analytes with concentrations of ten times the expected detection limit.

Quality control. Principles of quality assurance were an integral part of the laboratory investigations. Three control reagent blanks to monitor contamination and recovery of one control standard were routinely analyzed in the same manner as samples. The recovery data of control standard for quadruple IC system are presented in Table II. Quadruple IC system performance was monitored daily.

Reagents

Ultra pure water (18 M Ω cm resistivity at 25°C) was obtained by treating the tap water using reverse osmosis and ion-exchange columns (Millipore, modified Model RO 20 and Model Super Q).

Hydrochloric and sulfuric acids (J. T. Baker), 50% aqueous sodium hydroxide, methanol (Fisher Scientific), 2,3-diaminopropionic acid hydrochloride (DAP, Fluka), 50% aqueous solution of tetrabutylammonium hydroxide (Sachem, Austin, TX, USA) and other chemicals used were of analytical reagent-grade purity. Acetic, oxalic, citric, fumaric and phthalic acids and sodium formate (Fisher Scientific) and propionic, methanesulfonic, chloroacetic and benzoic acids and sodium dichloroacetate (Aldrich) were of highest available purity.

Anion stock standard solution was prepared from high purity salts (Fisher Scientific) and standardized *versus* NIST standard solutions (fluoride, chloride, bromide, nitrate, sulphate and phosphate). Stock solution of all nine cations was prepared from NIST standards. Ammonium standard solution was prepared from ammonium chloride (Fisher Scientific).

All eluents were prepared using helium degassed water. To avoid CO₂ pickup by sodium hydroxide eluents, eluents were prepared from 50% NaOH, which was pipetted from the middle of the bottle. He atmosphere was constantly applied over eluents. Composition of all eluents used in this work is presented in Table I.

TABLE II
RECOVERY DATA FOR CONTROL STANDARD

Reported results are the mean and standard deviation of 20 measurements of anion standard (F⁻, acetate, formate, Cl⁻ 0.2 μ g/ml; NO₂⁻ 0.4 μ g/ml; Br⁻, NO₃⁻, SO₄²⁻, oxalate 0.8 μ g/ml and PO₄³⁻ 1.0 μ g/ml), and cation standard (Li⁺ 0.2 μ g/ml; Na⁺ 1.0 μ g/ml; NH₄⁺ 0.8 μ g/ml; K⁺, Mg²⁺ 0.4 μ g/ml; Rb⁺, Cs⁺, Ca²⁺, Sr²⁺ 2.0 μ g/ml and Ba²⁺ 4.0 μ g/ml).

Ion	Recovery \pm S.D. (%)			Ion	Recovery \pm S.D. (%)
	IA Method	GA Method	GB Method		
F ⁻	N/A ^a	98.8 \pm 3.2	97.6 \pm 3.7	Li ⁺	95.9 \pm 5.8
Acetate	N/A	102.4 \pm 10.5	99.5 \pm 14.0	Na ⁺	93.6 \pm 6.4
Formate	N/A	95.8 \pm 8.1	94.4 \pm 7.6	NH ₄ ⁺	92.4 \pm 6.8
Cl ⁻	100.6 \pm 6.0	98.7 \pm 7.8	94.5 \pm 7.6	K ⁺	96.6 \pm 7.1
NO ₂ ⁻	100.8 \pm 4.5	97.1 \pm 3.0	94.4 \pm 6.4	Rb ⁺	96.5 \pm 4.7
Br ⁻	99.2 \pm 4.5	97.1 \pm 4.3	95.0 \pm 4.5	Cs ⁺	96.5 \pm 6.2
NO ₃ ⁻	98.3 \pm 3.6	98.1 \pm 4.5	97.9 \pm 5.5	Mg ²⁺	99.6 \pm 7.0
SO ₄ ²⁻	102.2 \pm 3.7	97.6 \pm 3.8	98.3 \pm 4.1	Ca ²⁺	100.6 \pm 7.0
Oxalate	99.7 \pm 3.3	97.9 \pm 2.7	97.5 \pm 4.2	Sr ²⁺	96.7 \pm 7.1
PO ₄ ³⁻	98.8 \pm 5.5	95.1 \pm 6.8	99.4 \pm 6.0	Ba ²⁺	93.4 \pm 11.5

^a N/A = not analyzed.

Filter extraction

Atmospheric aerosols collected on thin PTFE filters using virtual dichotomous samplers were obtained from the Pollution Measurement Division, River Road Environmental Technology Centre, Environment Canada. The samplers fractionated the aerosol into two aerodynamic size ranges yielding “fine” ($< 2 \mu\text{m}$) and “coarse” ($< 10 \mu\text{m}$) samples.

The elemental composition of collected atmospheric aerosols was nondestructively determined for forty elements using X-ray fluorescence (XRF). Then, the filters were placed in glass bottles for extraction. Particulates were extracted using water (19 ml) by sonication in an ultrasonic bath (Branson & Smithkline, Model Bransonic 42) for 30 min. Because some atmospheric aerosols and the PTFE are hydrophobic, the filters were wetted before addition of water with methanol (1 ml). The extracts were transferred to autosampler vials, which after pre-washing had contamination levels below 10 ng/ml for all ions determined. Analysis was carried out as soon as possible after extraction (within less than 24 h). The residue of extracts was stored at 4°C.

Stability of samples. Stability of aqueous extracts of atmospheric aerosols is one of important factors for correct analysis.

The preliminary study indicates that the extracts are relatively unstable. Some ions undergo chemical reactions (*e.g.* partial or complete oxidation of NO_2^- to NO_3^- and SO_3^{2-} to SO_4^{2-} in dependence on the pH of the extracts and other factors). Other ions are used up or generated in biochemical processes caused by the presence of microbiota (*e.g.* NO_3^- , NH_4^+). Biological activity in the samples containing carboxylic acids has been reported by Keene and Galloway [21]. Losses of formate and acetate were found in the extracts that were not treated with the biocide (chloroform). The extracts were therefore analyzed within less than 24 h after extraction.

The diluted working standard solutions are less sensitive to changes of concentration due to controlled pH and the absence of microbiota. They were nevertheless prepared freshly for each daily run. The effects of various preservation methods on stability of aqueous extracts of atmospheric aerosols will be reported in another paper [22].

RESULTS AND DISCUSSION

Analytical performance

The system stability was verified by constructing calibration curves from freshly prepared standard solutions every day that samples were analyzed. Within a six months period during which some 500 samples were analyzed, the relative standard deviations (R.S.D.) of slopes of the calibration curves were in the range 6–20%. Early eluting anions and cations in gradient elution (fluoride, acetate, formate, lithium and sodium) had an R.S.D. of retention time less than 5%. The R.S.D. of retention time was less than 2% for other cations and anions. The overall variability reflects uncertainties in preparation of standard solutions (gravimetric and volumetric errors), in standard stability (organic acids), in eluent variations from one batch to the next, and in instrument fluctuations (*e.g.* autoregeneration cartridge and/or suppressor exhaustion).

The long-term performance of the quadruple IC system was monitored by periodical re-analysis of standard solutions (as a rule one quality control standard solution was analyzed with each daily run). Recovery data of quality control standards are presented in Table II. The results indicate good system stability over the six months period.

Another measure of analytical performance involves interlaboratory comparison of water samples analyzed according to a “blind” protocol [23]. The data agree with interlaboratory median (Table III). The range of recovery was 96–106%. The analytical results were also precise as shown by the standard deviation of ten replicates.

The detection limits of the ten anions and ten cations studied using described system are listed in Table IV. It can be seen that all anions and cations have detection limit in the low ng/ml range. The concentrator column used in anion analysis improved the detection limits by about an order.

Filter results

Typical chromatograms of an extract of a fine and coarse atmospheric aerosol samples are shown in Fig 3. Chloride, sulphate, sodium and calcium are the major ions of coarse atmospheric aerosol extracts. All samples of fine atmospheric aerosol extracts contain sulphate and ammonium as major ions. Nitrate concentration was almost always only

TABLE III

DETERMINATION OF MAJOR ANIONS AND CATIONS IN WATER SAMPLE

Reported results are the mean and standard deviation of 10 replicates.

Ion	Inter-laboratory median ($\mu\text{g/ml}$) [23]	Found \pm S.D. ($\mu\text{g/ml}$)		
		IA Method	GA Method	GB Method
Cl^-	0.835	0.810 ± 0.021	0.850 ± 0.004	0.813 ± 0.016
NO_2^-	1.386	1.449 ± 0.029	1.443 ± 0.006	1.402 ± 0.037
NO_3^-	12.954	12.916 ± 0.182	12.733 ± 0.293	
SO_4^{2-}	22.740	24.052 ± 0.423	23.115 ± 0.201	
		CAT Method		
Na^+	0.207	0.199 ± 0.005		
NH_4^+	2.186	2.229 ± 0.019		
K^+	0.326	0.339 ± 0.011		
Mg^{2+}	2.640	2.624 ± 0.038		
Ca^{2+}	8.678	8.596 ± 0.296		

a small fraction of the sulphate concentration. It is possible to detect minor peaks in fine and coarse atmospheric aerosol extracts attributable to other cations [4] and anions. Some of the regularly reported anions are below the detection limits even after the concentration step.

Along with inorganic anions such as chloride, nitrite, nitrate and sulphate, organic anions were found in the extracts of atmospheric aerosols. Formate and acetate were usually present in higher concentration than other organic anions. They are mainly produced by anthropogenic (gas phase ox-

idation) and/or biogenic activity. They are often present in similar concentrations as sulphate and nitrate in urban areas on clear summer days [19]. As can be seen in Fig. 3 (chromatograms obtained after concentration of sample), fine and coarse atmospheric aerosol extracts contain other organic anions. Propionate, methanesulfonate and benzoate that have not yet been identified by other techniques were found in very low concentrations after preconcentration in some samples. The identification of other peaks will be the subject of future research.

TABLE IV

DETECTION LIMITS

Ion	Detection limit ($\mu\text{g/ml}$)				
	IA Method	GA Method	GB Method	Ion	CAT Method [4]
F^-	N/A	0.01	0.001	Li^+	0.005
Acetate	N/A	0.04	0.005	Na^+	0.025
Formate	N/A	0.03	0.002	NH_4^+	0.040
Cl^-	0.04	0.04	0.005	K^+	0.010
NO_2^-	0.02	0.01	0.002	Rb^+	0.040
Br^-	0.03	0.06	0.006	Cs^+	0.050
NO_3^-	0.03	0.01	0.006	Mg^{2+}	0.050
SO_4^{2-}	0.02	0.02	0.004	Ca^{2+}	0.050
Oxalate	0.04	0.02	0.002	Sr^{2+}	0.040
PO_4^{3-}	0.06	0.03	0.009	Ba^{2+}	0.400

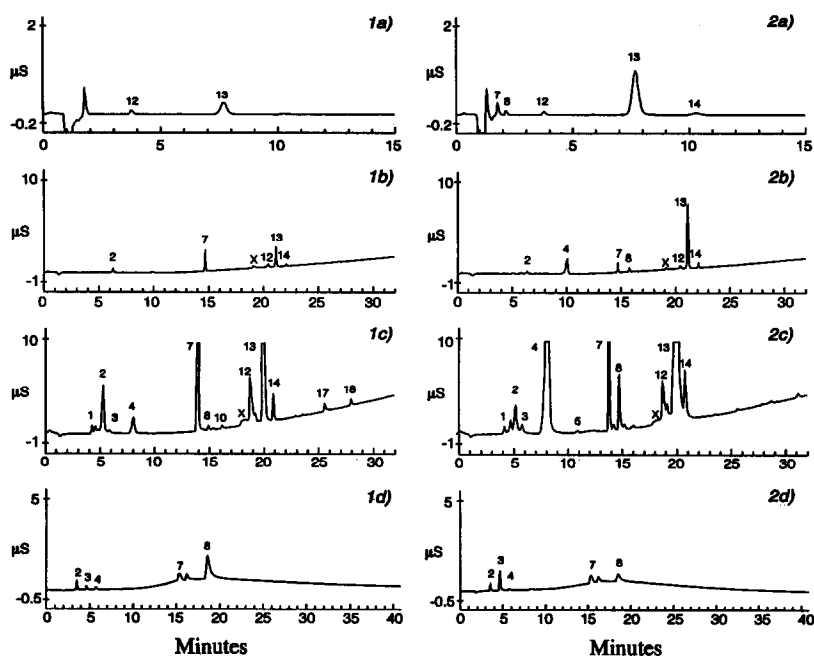


Fig. 3. Chromatograms of (1) coarse and (2) fine atmospheric aerosol extracts obtained by automatic quadruple ion chromatography system (a = anion isocratic IA; b = anion gradient GA; c = anion gradient with preconcentration GB and d = cation gradient CAT methods). Conditions are the same as those reported in Table I. Peaks: × = carbonate; others are the same as in Fig. 2.

Anion methods comparison study

The anions for which different elution methods can be compared are sulphate, chloride, nitrate and formate. Only these anions were present in sufficient amount to permit a quantitative anion methods comparison. The comparison of results obtained by isocratic and gradient (with and without preconcentration) elution is given in Table V. The results are

expressed as mean ratio of concentrations of analyte obtained by above mentioned elution methods. There was a close agreement (the range of the ratios was 0.94–1.03) between values obtained by the respective methods. Nitrate is the only exception caused by the sulphate interference. Sulphate was usually present in the samples at much higher concentration level than nitrate. Relative standard de-

TABLE V

ANION METHODS COMPARISON

All ratios are calculated from data where both concentrations were over quantitation limit.

Ion	IA vs. GA			GB vs. GA		
	Concentration range (µg/ml)	<i>n</i> ^a	Ratio ± S.D.	Concentration range (µg/ml)	<i>n</i> ^a	Ratio ± S.D.
Formate			N/A	0.1–1	82	1.02 ± 0.04
Cl ⁻	0.1–4	191	1.03 ± 0.08	0.1–2	137	0.94 ± 0.15
NO ₃ ⁻	0.1–6	255	0.97 ± 0.18	0.04–3	298	0.82 ± 0.14
SO ₄ ²⁻	0.07–8	460	1.03 ± 0.10	0.07–4	411	1.00 ± 0.10

^a *n* = Number of samples.

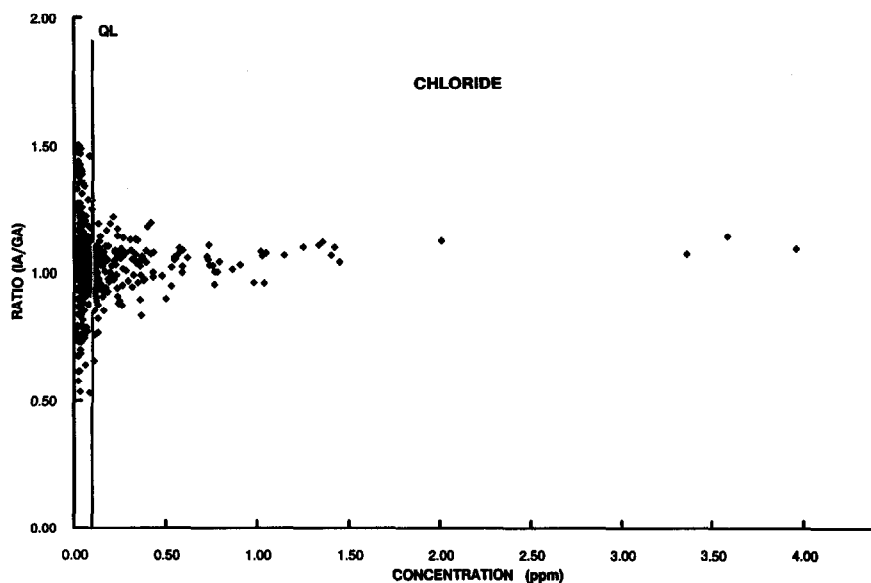


Fig. 4. Comparison of chloride determined by isocratic IA vs. gradient GA elution (QL = quantitation limit).

viations are better than 20%. Figs. 4 and 5 show the comparison of chloride and formate results obtained by isocratic and gradient (with preconcentration) methods vs. gradient method, respectively.

CONCLUSIONS

The described fully automated IC system is suitable for routine analysis of aqueous extracts of at-

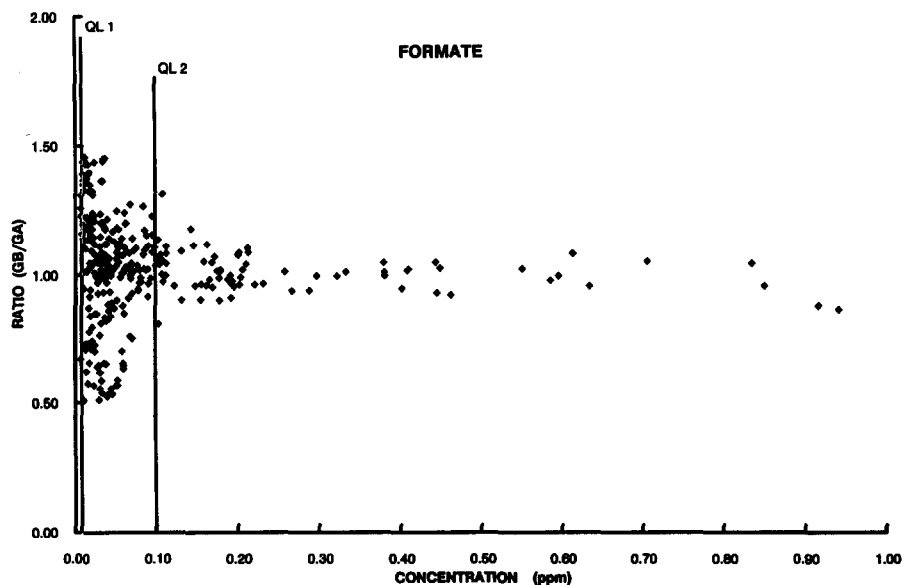


Fig. 5. Comparison of formate determined by gradient GB vs. gradient GA elution (QL1, QL2 = quantitation limits of GB and GA methods, respectively).

mospheric aerosols. It provides accurate and precise simultaneous multi-anion and multication determination capability. Other advantages of described IC system are the small sample volume required and the reduction of the probability of differential contamination of each sample. The stability of aqueous extracts of atmospheric aerosols is the limiting factor of time operation. Anion methods comparison has shown that there is good agreement between values obtained by the respective methods. Different approaches and changes, which will improve the method were found.

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