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Routine determination of major anions in atmospheric aerosols by capillary electrophoresis

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Abstract

Capillary electrophoresis (CE) with indirect UV detection utilizing a pyromellitate-based electrolyte was used for the routine analysis of major anions in atmospheric aerosols collected on filters with high-volume (Hi-Vol) samplers. The long-term reliability of the CE system was checked over an 8-month period during which over 2900 samples were analyzed. In addition, approximately 1100 samples were analyzed in parallel by ion chromatography (IC). It has been shown that acceptable analytical performance can be routinely obtained. The agreement between the CE and IC results is good, generally better than 20% at concentrations larger than 1 mg l^{-1}.

Keywords: Aerosols; Air analysis; Environmental analysis; Inorganic anions; Oxalate

1. Introduction

Over the past few years, capillary electrophoresis (CE) techniques have shown a tremendous growth in terms of efficiency, quantitation, and automation. By overcoming the systematic limitations and drawbacks, CE researchers are now achieving much better precision. When the ease of operation, efficiency and economy are considered, CE stands out in comparison to other separation techniques including ion chromatography (IC). Although CE has been utilized in many applications, widespread use of CE as a routine quantitative technique in environmental analysis has not yet appeared.

Previously reported work [1] demonstrated the potential advantages of CE with indirect UV detection for the determination of sulfate and nitrate in atmospheric aerosols collected on filters with high-volume (Hi-Vol) samplers, and compared this technique with photometric automated analysis and IC. The results suggested that the CE could be applied very advantageously for the routine determination of sulfate, nitrate and other anions in such samples. In addition, CE has been shown to be a viable alternative to photometric analysis as a result of its ability to perform rapid, efficient, and cost effective analyses in an automated format.

The present work shows results of the routine analysis of major anions in atmospheric aerosols using CE. The CE with indirect UV detection utilizing a pyromellitate-based electrolyte was applied [2,3]. Previously, the main method used in this laboratory for the determination of sulfate and nitrate in Hi-Vol sampled atmospheric aerosols was photometric analysis [4,5].

The long-term reliability of the CE system was

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checked over 8 months. The data that originated from the parallel analysis of CE and IC methods, in addition to the analysis of quality control samples, was used to monitor precision and accuracy.

2. Experimental

2.1. Apparatus

All CE measurements were performed on a Beckman P/ACE 2100 system (Fullerton, CA, USA) equipped with a multi-wavelength UV detector and an automatic sample changer. Data collection and analysis were carried out using Beckman GOLD software (v. 7.11).

Uncoated fused-silica capillaries (75 μm I.D., 50 cm to detector, 57 cm in total length) from Polymicro Technologies (Phoenix, AZ, USA) were utilized. The capillary was housed in a cartridge which allowed liquid cooling to maintain a constant capillary temperature at a chosen value during the run. In all experiments, the temperature of the capillary was maintained at 25±0.1°C.

Glass vials (5 ml) and polypropylene microvials (500 μl) were used for electrolytes and samples, respectively.

The IC determinations were carried out with a Dionex DX-300 IC system (Sunnyvale, CA, USA) equipped with an advanced gradient pump (AGP), an automated sample changer (ASM) and a conductivity detector (CDM-2). A 25-μl sample loop was used for the injection of samples. The separations of anions were performed on an IonPac AS4A column (250 mm×2 mm I.D.) with an IonPac AG4A guard column (50 mm×2 mm I.D.) using 1.7 m*M* $NaHCO_3$/1.8 m*M* Na_2CO_3 eluent at a flow-rate of 0.5 ml min^{-1}. Conductivity detection was carried out using an anion self-regenerating suppressor (ASRS-I) in the recycle mode. The chromatograph was controlled and the data was collected and processed on a personal computer using Dionex AI-450 software.

2.2. Reagents

All chemicals were purchased from Fisher Scientific (Ottawa, ON, Canada) in the highest purity available, and were used without further purification. The pyromellitate-based electrolyte was obtained from Dionex.

All standard solutions were prepared by diluting two mixed stock solutions (chloride, sulfate and nitrate: each 1000 mg l^{-1}; and bromide, nitrite and oxalate: each 500 mg l^{-1}).

Deionized water (>18 MΩ cm^{-1} resistance) obtained by treating tap water using reverse osmosis and ion exchange (Millipore, Model RO 20 and Model SuperQ, Millipore, Mississauga, Canada) was used in preparing all solutions.

2.3. Electrophoretic procedure

Electrophoretic separation was performed using a pyromellitate (PMA)-based buffer consisting of 2.25 m*M* pyromellitic acid (PMA), 6.5 m*M* NaOH, 0.75 m*M* hexamethonium hydroxide and 1.6 m*M* triethanolamine [2]. The pH was 7.7–7.9. Before use, the electrophoretic buffer was filtered through a 0.45-μm membrane Acrodisc syringe filter (Gelman-Sciences, Montreal, Canada). Every day, four 5-ml electrolyte filled glass vials were used: one vial was used for rinsing the capillary between runs, two vials were used for the separation of anions and one as a replacement of the electrolyte from the cathodic side at the point when approximately half of the samples were analyzed. Indirect UV detection was employed at 254 nm. A negative power supply (cathodic injection/anodic detection) of 30 kV was used and all injections were carried out by applying 0.5 p.s.i. pressure (1 p.s.i.=6894.76 Pa) for 10 s.

New uncoated capillaries were initially pretreated with the pressure feature of the Beckman P/ACE 2100 unit in the following manner: water wash for 5 min, a 0.5 *M* NaOH wash for 5 min, a 0.1 *M* NaOH wash for 5 min and a 5-min water wash. The capillaries were reconditioned daily with 0.1 *M* NaOH (5 min), then rinsed with deionized water (15 min) and with the used electrolyte (20 min). Separation of anions presented in Fig. 1 was carried out using a method that consisted of a 1-min rinse of the capillary with the running electrolyte prior to injection. After the final analysis of a sequence, the capillary was washed with water, followed by 0.1 *M* NaOH and water again for 5 min.

2.4. Analytical run

The CE instrument was calibrated daily followed by an analytical run of 45–55 samples. Six calibration standards at concentrations within the range 0.5–50 mg l^{-1} for chloride, sulfate and nitrate; and four calibration standards within the range 0.5–10 mg l^{-1} for bromide, nitrite and oxalate were used. All mixed standards (STD1–STD4) were prepared daily and STD5 and STD6 containing only chloride, sulfate and nitrate were prepared weekly. Duplicate injections of mixed standards were done and all sample analyses were performed as a single measurement. There were quality control (QC) samples with each batch of samples. Data was transferred from GOLD software (.rpt file) into the office personal computer for report compilation.

2.5. Quality control samples

Each set of atmospheric aerosol extracts was accompanied by one reagent blank, an internal quality control standard (a replicate of one of the calibration standards at the end of the daily run) and three external quality control samples (EQC) [6,7], which were analyzed in a manner identical to samples. Analytical data from these samples were used to verify that the analytical process is under control. Control charts were obtained from the analyses of these QC samples [8].

Identification of individual ions was based on the comparison of migration times of analytes with those of standard solutions. The sulfate peak was assigned to be a reference peak to determine the relative migration times of peaks within its zone. This allowed easy peak identification. When samples contained chloride at larger concentrations, this anion was used as a second reference peak. Calibration graphs were plotted based on the linear regression analysis of the corrected peak area (CPA).

2.6. Extraction procedure

Atmospheric aerosols, collected on PTFE-coated borosilicate glass fiber filters (Pallflex, TX40HI20WW, Putnam, CT, USA) using Hi-Vol samplers, were obtained from the Pollution Measurement Division, Environmental Technology Centre, Environment Canada.

Two discs, cut out from Hi-Vol filters, were placed in a 60-ml Nalgene-ware bottle. The filters were wetted with 1 drop of 30% Triton X-100 and then 25 ml of deionized water was added, and sonicated for 30 min in an ultrasonic bath (Branson and Smithkline, Shelton, CT, USA). Analyses were carried out the same day the extraction was performed. Before analysis the samples were filtered through a 0.45-μm membrane Acrodisc syringe filter.

3. Results and discussion

3.1. Long-term reliability of the CE system

Before calibration and data collection, the reliability of the CE system (stability of baseline, resolution) was verified. A representative electropherogram of a standard solution for the simultaneous determination of anions of interest is shown in Fig. 1a.

3.1.1. Calibration

Instrument response stability is a parameter which influences both accuracy and precision of the technique. The repeatability (between-batch precision) and linearity of the response of the analytes was verified by constructing calibration curves from freshly prepared standard solutions every day that samples were analyzed.

Within an eight-month period, during which over twenty-nine hundred samples were analyzed, very good stability of the CE system was obtained. During this period four capillaries were used. The relative standard deviations (R.S.D.s) of the response factor (slope of the calibration curves), measured in 56 calibrations, was less than 10% for all analyzed ions (Table 1). The correlation coefficients of obtained calibration curves always reach 0.999 or better. As can be seen in Table 2, very good repeatability of sensitivity defined as a response factor (concentration/corrected peak area) from capillary-to-capillary was obtained. Only using capillary IV, the sensitivity of analysis was slightly lower. This might be due to possible differences in an alignment of the capillary in the detection window.

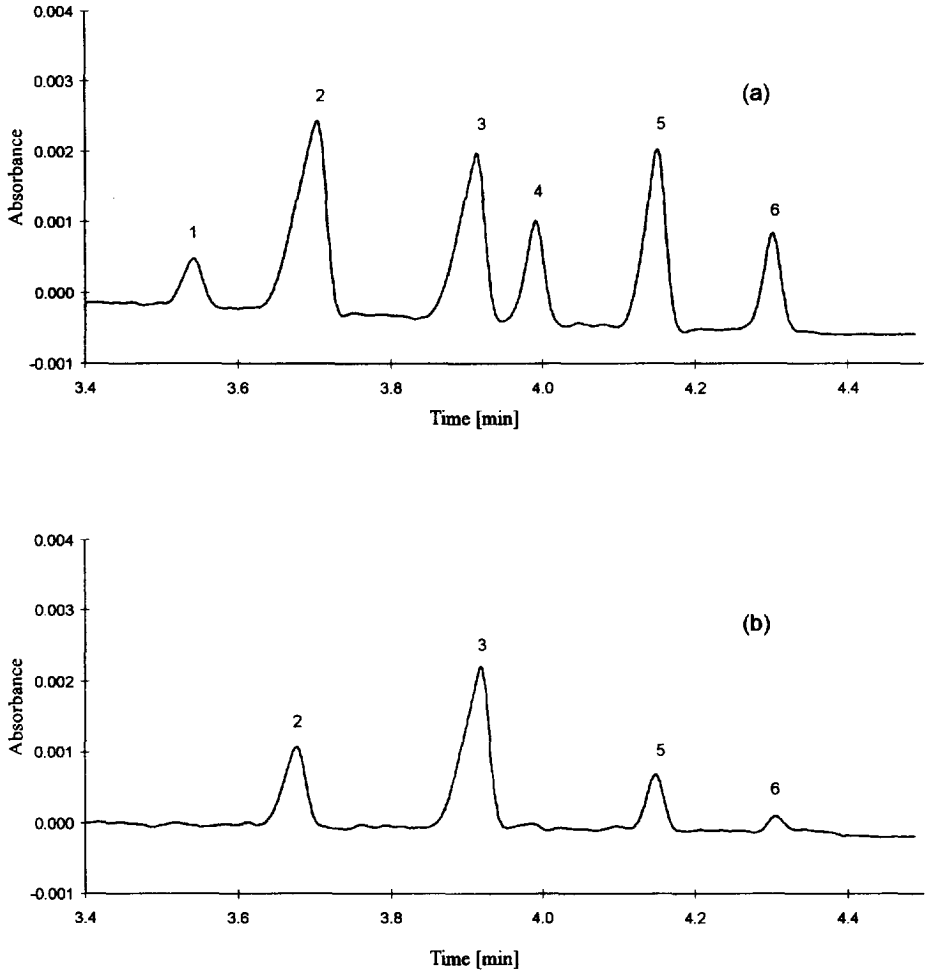

Fig. 1. Electropherograms of (a) anion standard mixture and (b) atmospheric aerosol extract solution. Peaks: 1=Br^-, 2=Cl^-, 3=SO_4^{2-}, 4=NO_2^-, 5=NO_3^-, 6=oxalate. For other conditions, see Section 2.

Table 1
Calibration characteristics and detection limit (DL)

	Response factor[a]		Intercept		R^2		DL[b] (mg l^{-1})
	Mean	R.S.D. (%)	Mean	S.D.	Mean	R.S.D. (%)	
Bromide	6.47	8.88	−0.01	0.09	0.9994	0.07	0.15
Chloride	2.83	7.93	−0.10	0.17	0.9998	0.03	0.07
Sulfate	3.91	9.49	−0.08	0.12	0.9999	0.02	0.13
Nitrite	3.82	10.01	−0.02	0.06	0.9996	0.04	0.12
Nitrate	4.88	7.59	−0.06	0.11	0.9997	0.05	0.09
Oxalate	3.59	9.65	−0.02	0.05	0.9997	0.05	0.11

[a] Response factor is defined as the slope of the concentration versus the corrected peak area (CPA) of anion injected.
[b] 3 S.D. of the 18 replicates of 0.5 mg l^{-1} standard.
Mean and standard deviations are obtained from 56 calibrations within 8 months.

Table 2
Comparison of response factor and migration time for sulfate using four capillaries

	n	Response factor[a]		Migration time (min)	
		Mean	R.S.D. (%)	Mean	R.S.D. (%)
Capillary I	13	3.70	5.19	4.02	2.98
Capillary II	16	3.80	8.70	3.78	5.41
Capillary III	8	3.84	6.38	3.82	4.26
Capillary IV	19	4.32	2.38	3.87	3.61

[a] Response factor is defined as the slope of the concentration versus the corrected peak area (CPA) of anion injected.

However, the best intra-day variability in the response factor (<3%) was obtained with that capillary (Fig. 2a). A loss of sensitivity (lower corrected peak area) occurred near the end of the use of capillary II was probably due to contamination. For this reason the capillary was changed and a controlled system was re-established as can be seen in Fig. 2a and b.

The overall variability reflects uncertainties in preparation of standard solutions (gravimetric and volumetric errors), in buffer variations from batch-to-batch, in instrument repeatability of the measurement of corrected peak area for calibration solutions (e.g. due to using different capillaries) and in random, non-identifiable errors.

The stability of the original calibration was monitored by reanalysis of one standard solution (internal quality control standard) at the end of each batch analysis. Corrected peak areas (CPA) ratio and percentage error of internal quality control sample (IQC) are presented in Table 3. The repeatability of the measurements of CPA for sulfate (Fig. 2b) and other anions were similar to the precision of the response factors (better than 9%). The between-batch precision of the CPA ratios of the IQC samples was between 3–7% and show the status of the instrument which is independent of the capillary and calibration procedure used. These results indicate very good system stability within daily runs.

3.1.2. Migration time

Batch-to-batch repeatability in migration time of IQC samples using four capillaries is shown in Fig. 2c and Table 3. The R.S.D was found to be better than 5% for all analyzed anions. The average deviation for sulfate from capillary-to-capillary was better than 0.1 min as shown in Table 2.

The precision of migration time of the atmospheric aerosol extracts analyzed within one batch was found to be in the range 1–2%, although minor shifts in the migration time become evident over several consecutive separations. This shift is negligible from run-to-run but obvious when comparing analyses separated at the beginning and at the end of daily operation. This shift is likely the result of the dependence of migration time upon the concentration of the analytes and how long the electrophoretic buffer was used. Since all samples contained sulfate as a major anion, this anion was selected as a reference ion for easier peak identification as well as correction for any migration shifts. When the electrolyte will be replaced more often by a fresh solution (not once as in this study), the improvement in the precision of migration time should be obtained.

3.1.3. Stability of the capillary

As mentioned above, 4 capillaries were used within 8 months. Reproducibility and capillary lifetime for this particular application was very good. The capillary could be used for at least 1500 analyses (e.g. capillary IV) without a significant change in performance (Fig. 2, Table 2). Capillary II was changed, because the loss of sensitivity was observed as mentioned above. The lifetime of the other capillaries were shorter due to breaking. In general, it was found that the stability of capillaries was better, when they were used on a consistent basis.

3.1.4. Accuracy, precision and quality control

The aim of any QC system is to detect small shifts in calibration at any early stage as well as gross bias in each batch. In order to evaluate the analytical performance of the used CE method, three external quality control (EQC) samples, used for round robin studies [6,7], at different anion concentrations were analyzed with each batch of study. Relative to detection limits, the concentration ranges were as follows: chloride, 4–850 times; sulfate, 10–350 times; nitrate, 13–100 times. This protocol has provided information on batch bias and as a basis for establishing quality control data to validate each analysis over a period of the 8 months. In addition,

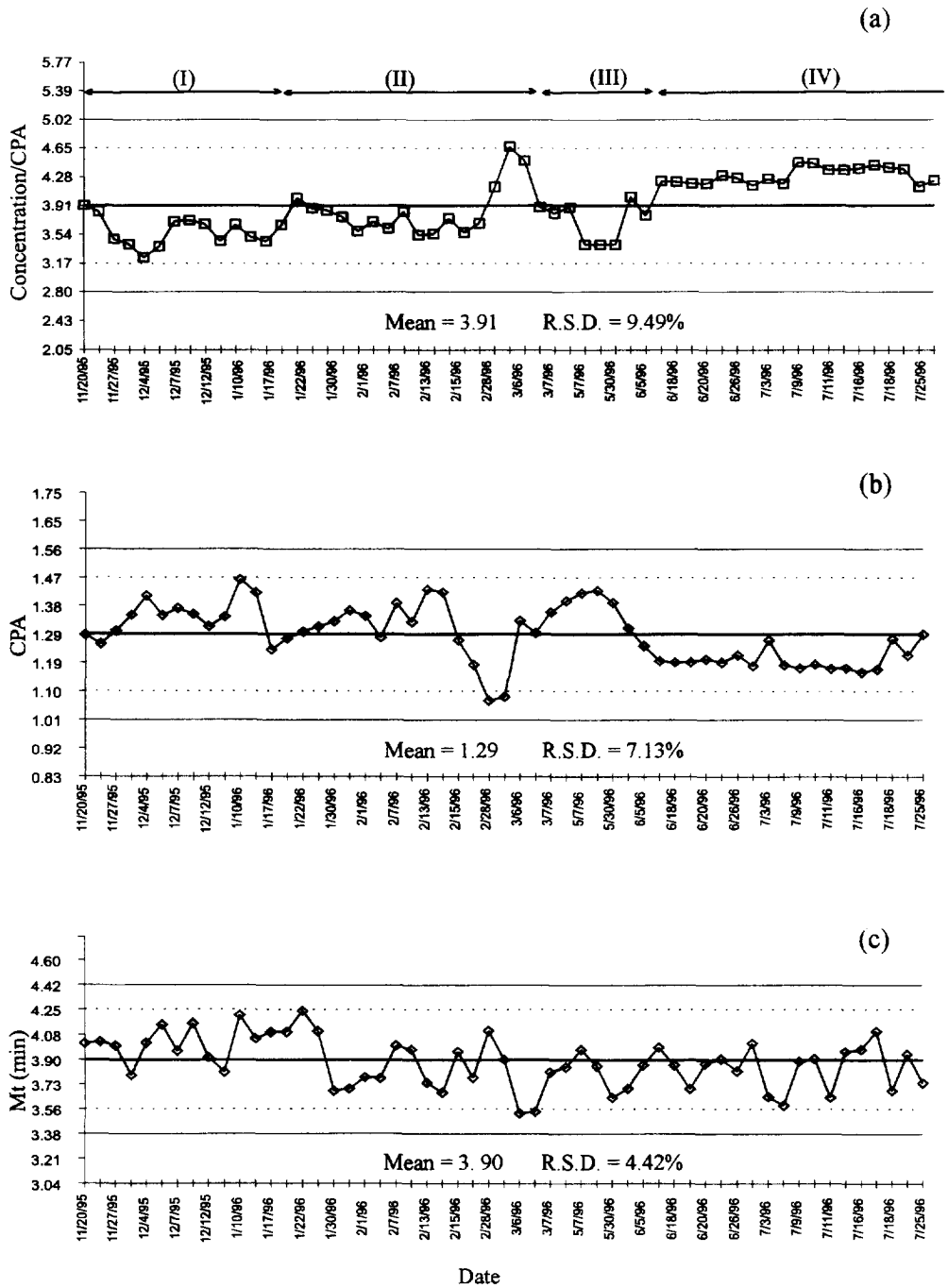

Fig. 2. Repeatability of (a) the response factor (slope of calibration curve), (b) the corrected peak area and (c) the migration time for sulfate (5 mg l^{-1}) obtained within an 8-month period using 4 capillaries (I–IV).

Table 3
Internal quality control sample

	Migration time (min)		Ratio[a]		Error (%)[b]	
	Mean[c]	R.S.D. (%)[c]	Mean[c]	R.S.D. (%)[c]	Mean[c]	R.S.D. (%)[c]
Bromide	3.52	3.94	0.9894	6.97	+0.16	7.18
Chloride	3.68	4.13	1.0012	3.32	+0.72	4.99
Sulfate	3.90	4.42	1.0044	3.83	−0.15	3.66
Nitrite	3.97	4.46	0.9903	4.98	+0.23	5.44
Nitrate	4.13	4.62	0.9951	3.99	+0.41	3.42
Oxalate	4.29	4.83	0.9876	6.49	−1.35	5.83

[a] Ratio of the corrected peak area of STD3 at the end (IQC) and at the begining of the daily run.
[b] 100×(Mean concentration − design concentration)/design concentration.
[c] Mean and standard deviations are from 55 measurements obtained during an 8 month period of the internal quality control standard solution (Br^-, NO_2^-, Ox^{2-}: each 2 mg l^{-1}; Cl^-, SO_4^{2-} and NO_3^-: each 5 mg l^{-1}).

the obtained results contributed to stimulating the analysts to solve technical problems and improve laboratory practice.

Examples of the control charts obtained are shown in Fig. 3. Warning (2 S.D.) and control limits (3 S.D.) were calculated from the whole data set. Within the 8-month period, the increase in the precision due to improvement of laboratory practice was observed. The best results were observed for sulfate, followed by nitrate and chloride (Table 4). A slight increase in the concentrations of sulfate and chloride within time was observed, probably due to either contamination (chloride) or calibration errors. The spread of analytical data for the lower concentration EQC sample is larger, especially for chloride at concentrations close to the quantitation limit. As can be seen in Table 4, the data agree with the interlaboratory median values within 7% for reported anions. Only chloride results, at concentrations close to the quantitation limit, were higher. In general, the accuracy and precision of the measurements become worse at concentrations closer to the quantitation limit, as expected.

Within-batch precision values are slightly lower than those achieved on a routine analytical run (Table 4). It is known that within-batch data is always superior to between-batch precision [9]. Therefore, within batch QC data does not provide a realistic data set from which QC limits could be established to detect bias. An excellent evaluation of quality control including control of errors in ion chromatography applied to environmental research was reported by Rowland et al. [9].

3.2. Correlation of CE and IC results

During the implementation of CE for the routine laboratory analysis of major anions in Hi-Vol sampled atmospheric aerosols, approximately 1100 samples were analyzed in parallel using ion chromatography (IC). Chloride, sulfate, nitrate and oxalate are the major ions in these samples (Fig. 1b). Previously, sulfate and nitrate in such samples were analyzed using photometric methods [1].

To investigate the accuracy further, the results obtained by the CE method were compared with those of the recognized IC method. Linear least-squares adjustment of each set of results yielded the values (±95% confidence limits, [10]) that are presented in Table 5. As can be seen very good correlation exists for sulfate, nitrate and chloride with the regression curves having slopes close to 1 and high coefficients of correlation. A relatively higher deviation was observed for oxalate, which is present in the gross samples at much lower concentrations compared to other anions.

In addition to regression procedures, other visual evaluation is recommended [11–14] for method comparison. In this work, a quantitative deviation between the two methods was calculated in terms of the relative percentage difference (RPD) between results as follows:

$$\mathrm{RPD}(\%) = (X_{\mathrm{CE}} - X_{\mathrm{IC}})/0.5(X_{\mathrm{CE}} + X_{\mathrm{IC}})$$

where X_{CE} and X_{IC} are the measurements of anion concentrations of the same filter extracts but using CE and IC, respectively.

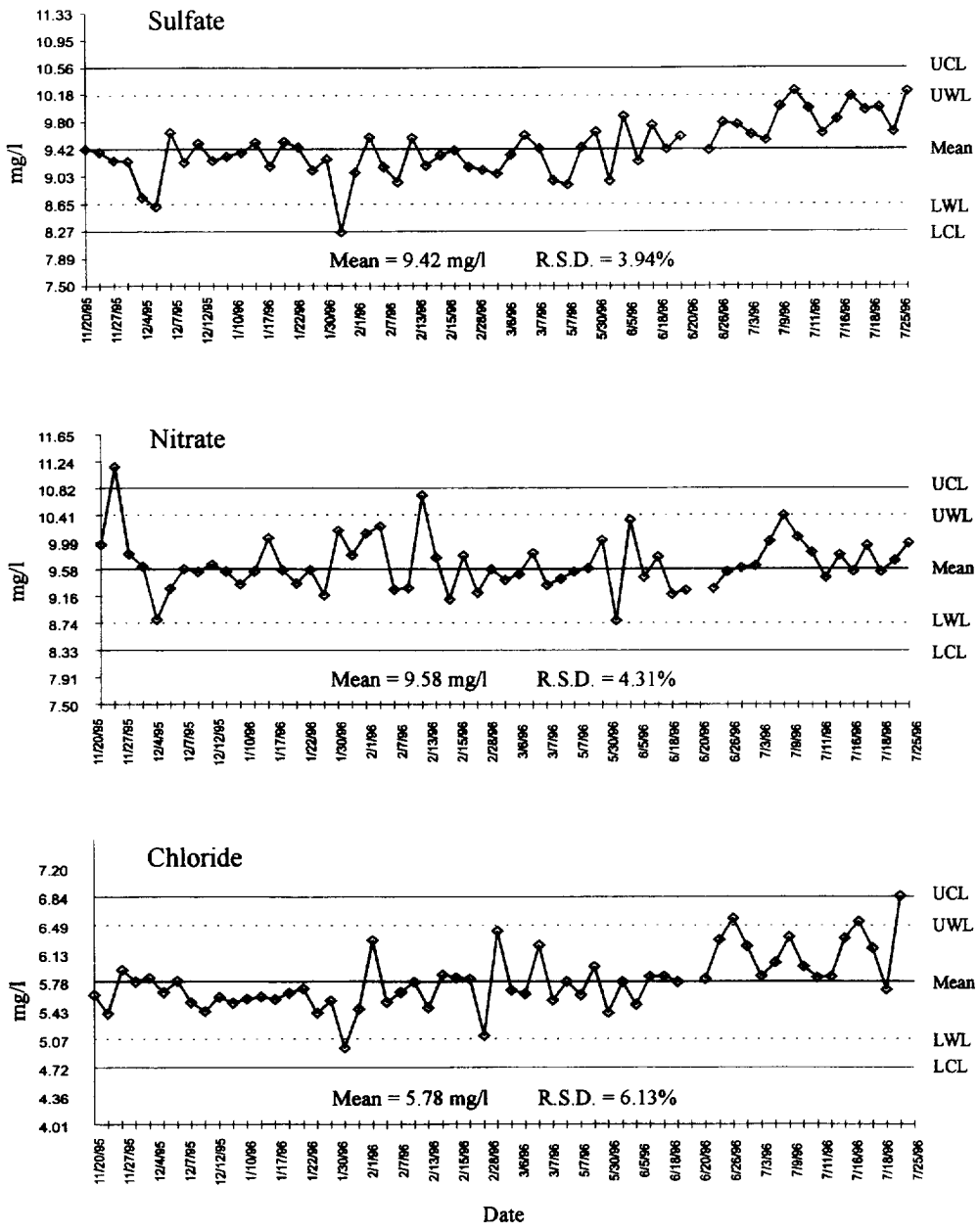

Fig. 3. Examples of control charts. UCL and LCL = upper and lower control limits (±3 S.D.); UWL and LWL = upper and lower warning limits (±2 S.D.).

The RPDs plotted against the mean of the two obtained values for four detected anions are shown in Fig. 4. As shown in Fig. 4a, the RPD of sulfate is found to be less than ±15% at concentrations greater than 1.0 mg l^{-1}. Above 25 mg l^{-1}, sulfate generally shows excellent agreement between CE and IC results, with differences less than 5% relative. Nitrate shows slightly larger differences between CE and IC results, although agreement is within 10% at concentrations greater than 5 mg l^{-1}. For chloride,

Table 4
Quality control samples

	Inter-laboratory median [6,7] ($mg\ l^{-1}$)	Within-batch[a]		Between-batch		
		Error (%)[b]	R.S.D. (%)	n[c]	Error (%)[b]	R.S.D. (%)
Chloride	0.30	−13.14	9.87	44	−20.60	26.61
	5.41	−2.35	0.69	58	6.88	5.78
	59.6	−0.64	0.61	58	0.15	3.95
Sulfate	1.31	−6.33	5.20	44	3.67	5.23
	9.01	1.23	1.63	58	4.53	3.94
	46.2	−0.19	1.36	58	3.80	4.86
Nitrate	1.14	−8.65	5.58	44	2.46	8.92
	1.77	−6.65	3.68	58	4.84	6.49
	10.0	6.71	0.97	58	−4.33	4.37

[a] Mean and standard deviation from 9 replicates.
[b] 100×(Mean concentration − inter-laboratory median)/inter-laboratory median.
[c] Number of measurements.

comparatively large differences are observed between CE and IC results at concentrations between 1.5–7.5 $mg\ l^{-1}$ (±50%), while above 7.5 $mg\ l^{-1}$, the RPD was found to be less than ±10%. The significant difference of RPD in chloride measurements is likely the result of the calibration problems at this concentration range. Some definite outlier results were present too. The study to find the source of these differences is under investigation. Oxalate, which is present at much lower concentrations than other anions in the extracts, shows RPD values within ±20% at concentrations larger than 1 $mg\ l^{-1}$.

4. Conclusions

The results of this work show the acceptable analytical performance of the CE system using the PMA-based buffer in the routine analysis of major ions in atmospheric aerosols. The highly efficient separation of CE with short analysis time and cost effective analyses in an automated format makes it an excellent tool for such analysis. Comparable results can be obtained using CE and IC. For most observations, the measurements from the two applied methods were in very good agreement at higher concentrations. However, for more diluted solutions (below 1 $mg\ l^{-1}$, about 7 times the CE detection limit), poorer agreement was observed, as expected. This is attributed to the poorer sensitivity of the CE method and possible calibration errors (larger intercept). As concentrations increase, the differences stabilize to about ±20% and down to ±5% for the anions at concentrations greater than 20–25 $mg\ l^{-1}$.

Attempts to improve within- and between-day precision and accuracy, especially at low levels, for

Table 5
Statistical analysis results (±95% confidence limit) [10]

Anion	Concentration range ($mg\ l^{-1}$)	n	Slope[a] (A)	Intercept[a] (B)	R^2
Sulfate	0.43–63	1030	0.998±0.001	−0.053±0.014	0.9981
Nitrate	0.30–34	783	1.008±0.002	−0.046±0.005	0.9980
Chloride	0.24–63	360	1.006±0.003	−0.101±0.025	0.9966
Oxalate	0.38–3	643	0.940±0.058	0.008±0.009	0.9350

[a] (CE)=A×concentration (IC)+B ($mg\ l^{-1}$).
All results were over quantitation limits.

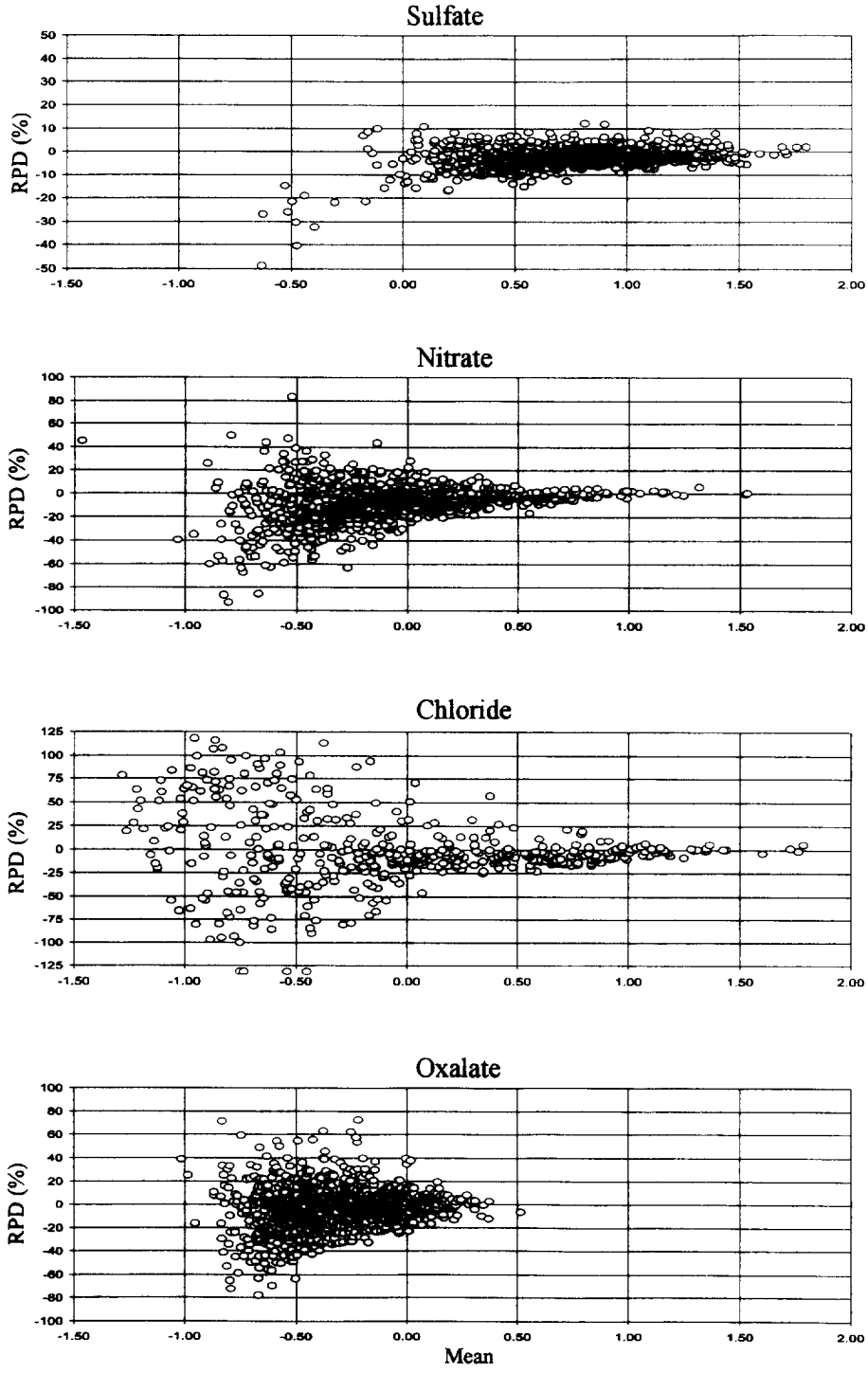

Fig. 4. Visual evaluation for the comparison of the results obtained by CE and IC methods. RPD-relative percentage difference between results. In order to observe the spread at low concentrations (around zero), the values of the mean concentrations have been transferred to a logarithmic scale.

the routine monitoring of major ions in atmospheric aerosols using CE, are in progress. With these and other demonstrations, along with additional improvements, the authors hope that CE will be accepted as a routine assay in environmental analyses.

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