

# Comparison of capillary zone electrophoresis with ion chromatography and standard photometric methods for the determination of inorganic anions in atmospheric aerosols

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## Abstract

The capillary zone electrophoresis (CZE), ion chromatography and photometric techniques were compared for the analysis of nitrate and sulphate in high-volume sampled atmospheric aerosols. The CZE method with indirect UV detection utilizing a pyromellitate-based electrolyte was used. The comparative evaluation included response stability of instruments, detection limits, accuracy, precision, analysis time and other operational considerations. Statistical analysis of the results indicated that there was no evidence for systematic differences between the three techniques. The results suggest that CZE can be applied very advantageously in an anion analysis in atmospheric aerosols.

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## 1. Introduction

The determination of inorganic acid species, in addition to other pollutants is a part of monitoring and assessing the ambient air quality in Canada under the National Air Pollution Surveillance (NAPS) network.

Sulphate and nitrate are the major anionic constituents of the atmospheric aerosols collected on filters with high-volume (Hi-Vol) samplers. Measurements of these species in atmospheric aerosols, provide information connected to acid rain. To date, the main method used in this laboratory for the determination of sulphate and nitrate in such samples is photometric analysis with an automated wet chemistry system

(AWC) [1–3]. Photometric analysis of anions is being replaced by ion chromatography (IC), which offers advantages in terms of sensitivity and fully automated multiple analyte determination in a single assay. During the past decade IC, using chemically suppressed conductivity detection, has become established as a powerful analytical tool for determination of anions and cations in environmental samples including atmospheric aerosols [4–6].

IC is not the only method for separating ionic species. Capillary zone electrophoresis (CZE), a form of capillary electrophoresis (CE) where separation is mainly based on differences in solute size and charge at a given pH, has successfully been introduced as a new separation technique for the analysis of inorganic and organic ions [7,8]. Most published work is based on the

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indirect photometric detection that can be used for the detection of compounds that have no optical absorbance. High efficiency, versatility, speed and economy of analysis are among the many attributes that promoted the application of CE in many real samples [9–18]. This technique also complements IC, and thus provides the confirmation of IC results [12,16]. The introduction of CE technique in an environmental analytical laboratory allows methods and results validation.

This paper presents the potential advantages of CE for the determination of sulphate and nitrate in atmospheric aerosols and compares this technique with photometric automated analysis and IC. The comparative evaluation includes detection limits, linearity, accuracy, precision, correlation between the results, analysis time and other operational considerations.

## 2. Experimental

### 2.1. Photometric automated wet chemistry (AWC)

The Technicon (Tarrytown, NY, USA) Auto-Analyzer II used in this study was a two flow path automated photometric system consisting of a 40 samples per tray sample changer, a peristaltic proportioning pump drawing up the reagents and samples through the system, a network of tubing, bubble injectors and mixing coils, two photometric detectors and a dual-pen chart recorder.

The following methods for photometric analysis with an AWC system were used: sulphate at 460 nm indirectly by releasing methylthymol blue (MTB) from a barium–MTB complex [1,2] and nitrate at 520 nm after reduction to nitrite as an azo dye [3].

The instrument was calibrated independently for each analyte with standard solutions at six different concentrations within the range 0.25–2.0 mg N/l for nitrate and 5–60 mg/l for sulphate. The standard solutions were prepared weekly. Calibration graphs were plotted based

on the quadratic regression analysis of peak height measured manually.

### 2.2. Multi-dimensional IC

All IC equipment, columns and software used in this study were from Dionex (Sunnyvale, CA, USA). The multi-dimensional IC system [5,6] contained three ion chromatographs (Model 4500i) with gradient pumps (GPM), an ion chromatograph (Model DX-300) with an advanced gradient pump (AGP), an automated sample changer (ASM), one micromembrane chemical suppressor (AMMS-II 2 mm), three self-regenerating suppressors (ASRS-I 4 mm, CSRS-I 4 mm), four microconductivity detectors (CDM-2), one autoregeneration accessory (AutoRegen), trap, concentrator, guard and analytical columns. Two personal computers (IBM, PS 2/70) contained the operating and processing software (AutoIon 450) were connected to the equipment through interface modules (ACI).

Aqueous extracts of atmospheric aerosols were analyzed for 14 inorganic and organic anions and 11 inorganic cations using multi-dimensional IC. Four methods were applied: anion isocratic (IC-IA), anion gradient without (IC-GA) and with concentrator column (IC-GB) and cation gradient (IC-CAT). In this work, only isocratic and gradient anion IC methods were used for the comparative study. Separation of anions by isocratic elution was performed on an IonPac-AS4A column with an IonPac-AG4A guard column with  $\text{CO}_3^{2-}/\text{HCO}_3^-$  eluent, and by gradient elution on IonPac-AS10 column with an IonPac-AG10 guard column with NaOH eluent. Chromatograms of standard solutions are shown in Fig. 1.

Five standard calibrations were used for analysis of anions. Calibrations were performed over the range of concentrations expected in the samples (nitrate 0.4–16 mg/l, nitrite 0.1–4 mg/l and sulphate 0.4–80 mg/l).

Peak areas with linear least squares regression were used in anion gradient method, and with quadratic regression in anion isocratic elution.

Identification of individual ions was based on

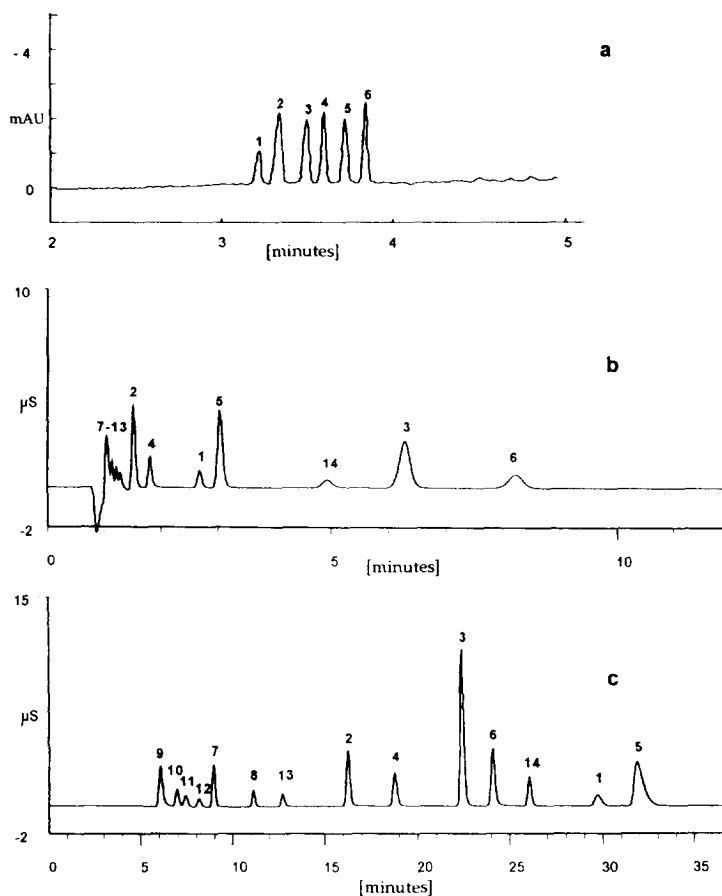


Fig. 1. Separation of an anion mixture standard by (a) CE, (b) isocratic IC and (c) gradient IC after baseline subtraction. Conditions: (a) electrolyte: 2.25 mM pyromellitic acid, 6.5 mM NaOH, 0.75 mM hexamethonium hydroxide, 1.6 mM triethanolamine, pH 7.7–7.9; capillary: 57 cm (50 cm to detector)  $\times$  75  $\mu\text{m}$  I.D. fused silica; voltage: 30 kV, negative polarity, detector side anodic; detection: indirect UV at 254 nm; injection: pressure, 10 s; (b) columns: IonPac-AG4A and IonPac-AS4A (2 mm); eluent: 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate; flow-rate: 0.5 ml/min; suppressor: AMMS-II, 2 mm; regenerant: 25 mM sulphuric acid; regenerant flow-rate: ca. 5 ml/min; detector: conductivity; injection volume: 25  $\mu\text{l}$ ; (c) columns: IonPac-AG10 and IonPac-AS10 (4 mm); eluents: E1 = 20 mM NaOH, E2 = 200 mM NaOH; flow-rate: 1.0 ml/min; suppressor: ASRS-I, 4 mm, recycle mode; detector: conductivity; injection volume: 100  $\mu\text{l}$ . Peaks: 1 = bromide; 2 = chloride; 3 = sulphate; 4 = nitrite; 5 = nitrate; 6 = oxalate; 7 = formate; 8 = methanesulphonate; 9 = fluoride; 10 = acetate; 11 = propionate; 12 = butyrate; 13 = chloroacetate; 14 = phosphate.

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

### 2.3. Capillary electrophoresis

A P/ACE 2100 CE system (Beckman Instruments, Fullerton, CA, USA) with a multi-wavelength UV detector, an automatic sample changer and a liquid thermostated capillary cartridge [capillary 57 cm (50 cm to detector)  $\times$  75

$\mu\text{m}$  I.D.] and a personal computer (IBM PS/2 70) utilizing a Beckman Gold System (version 7.11) software for instrument control and for data collection and processing were used. Glass electrolyte vials (5 ml) and 30-sample carousel with 100- $\mu\text{l}$  polyolefin microvials were used.

The running electrolyte consisted of 2.25 mM pyromellitic acid (PMA), 6.5 mM NaOH, 0.75 mM hexamethonium hydroxide (HMOH) and 1.6 mM triethanolamine (TEA) [8,16]. The pH

was between 7.7 and 7.9. Electrolyte was filtered by using a plastic syringe with a 0.22- $\mu\text{m}$  syringe PTFE filter and degassed daily by creating a vacuum inside the syringe.

The capillary was reconditioned daily with 0.1 M NaOH (10 min), then rinsed with deionized water (5 min) and with the used electrolyte (5 min). Separation of anions presented in Fig. 1a was carried out using a method that consisted of a 1-min rinse of capillary with the running electrolyte prior to injection. The operating voltage of 30 kV with the reverse-polarity mode was applied. All injections were achieved using a 10 s pressure injection technique. Indirect UV detection at 254 nm was used.

Identification of individual ions was based on the comparison of migration times of analytes with those of standard solutions. All mixed standard solutions for the CE work were prepared every day that samples were analyzed. Calibrations were performed over the range of concentration expected in the samples. Six calibration standards were used at concentrations within the ranges 0.4–80, 0.4–16 and 0.1–4 mg/l for sulphate, nitrate and nitrite, respectively. Calibration graphs were plotted based on the linear regression analysis of the corrected peak area.

#### 2.4. Reagents

All chemicals were purchased commercially from either Fisher Scientific (Ottawa, Canada), Technicon or Kodak (Rochester, NY, USA) in the highest purity available, and were used without further purification. Pyromellitate based electrolyte was obtained from Dionex.

All solutions were prepared with deionized water (18 M $\Omega$  cm) obtained by treating tap water using reverse osmosis and ion exchange (Millipore, Model RO 20 and Model SuperQ, Bedford, MA, USA).

#### 2.5. 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 100-ml beaker. The filters were wetted with two drops of 30% Triton X-100 and then 25 ml of deionized water were added. The beakers were then covered with Parafilm 1“M” and extracted for 30 min in an ultrasonic bath (Branson and Smithkline, Shelton, CT, USA). Analysis was carried out as soon as possible after extraction (within less than 24 h).

#### 2.6. Sample pretreatment

The only sample pretreatment was filtration by using a glass syringe with a 0.22- $\mu\text{m}$  syringe PTFE filter connected.

#### 2.7. Analysis of atmospheric aerosols

The number of Hi-Vol filter disc pairs that was analyzed for sulphate, nitrate and nitrite by CE, multi-dimensional IC and photometric AWC was 145. The parallel analysis of atmospheric aerosol extracts on each system was performed by different analysts.

#### 2.8. Quality assurance

Each set (22) of atmospheric aerosol extracts was accompanied by two reagent blanks, an internal quality standard (a replicate of one of the standards used for calibration at the end of the daily run) and two external quality control samples [19] which were carried through the entire analytical scheme in a manner identical to samples.

### 3. Results and discussion

#### 3.1. Performance characteristics

##### *Response stability of instruments*

Instrument response stability is a parameter which influences both accuracy and precision of the technique. Stability of instruments was ver-

ified by constructing calibration curves from standard solutions every day when samples were analyzed.

Within a seven working days during which some 150 samples were analyzed, very good stability of CE and IC systems was obtained. The relative standard deviations (R.S.D.s) of the linear coefficient were less than 5% for both the IC and CE systems (Table 1). Correlation coefficients of obtained calibration curves were in the range 0.9991–0.9999. Worse precision of calibration characteristic from run to run was obtained for the photometric analysis with the AWC system. The overall variability in the photometric AWC system within 7 days reflects mainly uncertainties in error due to manual measurement of peak heights.

#### Migration and retention time stability

With the exception of sulphate analyses by isocratic IC elution, the precision of retention times of anions in standard solutions was less

than 1% within 7 running days (Table 1). The R.S.D.s of analyte migration times in standard solution by CE was found to be less than 3% between daily runs (Table 1). However, analyte migration times in CE are more strongly affected by the sample matrix than in IC. The high resolution of CE causes a slight change in migration time to be more significant with CE than IC. Because of the sample matrix effect on the analyte migration time, relative migration times with respect to a reference peak should be used with CE.

#### Detection limits

The method detection limits were calculated by analyzing dilute solutions. They were taken as three times the standard deviation of twenty replicate analyses of the sample containing analytes with the concentration about ten times higher than the estimated detection limit, the latter being the concentration giving a signal-to-noise ratio of 3.

The lowest detection limits were obtained by

Table 1  
Performance of tested techniques

Parameter	Analytes	Photometric AWC	IC		CE
			Isocratic	Gradient	
Calibration range (mg/l)	NO <sub>3</sub> <sup>-</sup> (N)	0.25–2.00	0.09–4.00	0.09–4.00	0.09–4.00
	SO <sub>4</sub> <sup>2-</sup>	5–60	0.4–80	0.4–80	0.4–80
Linear coefficient (R.S.D., %) <sup>a</sup>	NO <sub>3</sub> <sup>-</sup> (N)	21.24	0.91	1.17	3.33
	SO <sub>4</sub> <sup>2-</sup>	14.99	1.30	0.66	4.20
Linearity R <sup>2</sup>	NO <sub>3</sub> <sup>-</sup> (N)	0.9949	0.9999	0.9991	0.9997
	SO <sub>4</sub> <sup>2-</sup>	0.9972	0.9998	0.9999	0.9997
Retention time (R.S.D., %)	NO <sub>3</sub> <sup>-</sup> (N)	Not analyzed	0.85	0.39	2.65
	SO <sub>4</sub> <sup>2-</sup>	Not analyzed	1.78	0.26	2.46
Detection limit (mg/l)	NO <sub>3</sub> <sup>-</sup> (N)	0.056	0.003	0.011	0.035
	SO <sub>4</sub> <sup>2-</sup>	0.712	0.013	0.026	0.154
Number of samples per day		100	85	22	100
Number of analytes per day		200	595	550 <sup>b</sup>	600

<sup>a</sup>Reported results are obtained from 7 measurements within 7 working days.

<sup>b</sup>For multi-dimensional IC.

IC followed by CE and photometric AWC (Table 1).

### 3.2. Accuracy and precision

To ensure the accuracy of the CE, IC and AWC results, external quality control samples (EQC) were used [19]. The data agree with the interlaboratory median values within 6% for reported anions at higher concentration and determined by the used analytical techniques (Table 2). Only sulphate results obtained by the photometric AWC method were higher. The accuracy and precision of the measurements becomes worse at concentration closer to quantitation limit, as expected. It can be seen that the photometric AWC methods are also less precise over-all than CE and IC methods. Specifically, the photometric AWC has inferior reproducibility for sulphate at lower concentration.

#### Correlation of CE, IC and photometric AWC results

The statistical analysis was performed to test the accuracy of the CE method when applied to

the determination of nitrate and sulphate in atmospheric aerosols. Because the photometric AWC method measures total concentration of nitrate and nitrite (results are reported as nitrogen), nitrate and nitrite results obtained by IC and CE and expressed as nitrogen were added. The concentration of nitrite in all samples was always lower than nitrate concentration.

The relationship between concentrations ( $C$ ) of analyzed anions obtained by the respective methods were evaluated by linear correlation [20] in the form:

$$C \text{ (CE or IC)} = aC \text{ (AWC)} + b \text{ (mg/l)}$$

or

$$C \text{ (CE)} = aC \text{ (IC)} + b \text{ (mg/l)}$$

as shown in Figs. 2 and 3 and Table 3. This statistical analysis showed no evidence of either relative or fixed bias between the three techniques, and the CE method is considered to be acceptable for the purpose of this type of measurement. The best correlation of results was obtained by both IC methods (Table 3).

The results were also expressed as median and

Table 2  
Quality control sample

Analyte	Inter-laboratory median [19] (mg/l)	Method	Error (%) <sup>a</sup>	R.S.D. (%) <sup>b</sup>
Nitrate (N)	2.450	AWC	+ 0.7	4.57
		IC-IA	+ 0.79	1.18
		IC-GA	- 4.05	0.63
		CE	+ 1.45	1.07
Sulphate	6.926	AWC	+ 9.47	4.01
		IC-IA	- 5.85	0.5
		IC-GA	- 0.79	0.71
		CE	+ 1.94	1.93

IC-IA, IC-GA = Isocratic and gradient IC elution, respectively.

<sup>a</sup>100 × (Mean concentration - inter-laboratory median concentration)/inter-laboratory median concentration.

<sup>b</sup>From 7 measurements obtained within 7 working days.

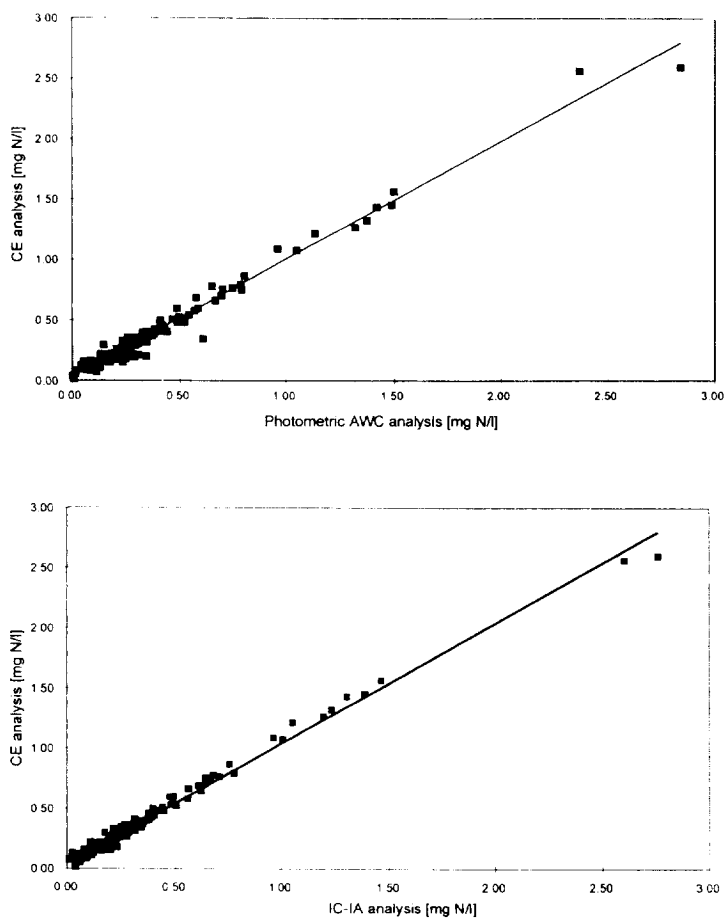


Fig. 2. Comparison of the results for the determination of nitrate plus nitrite in atmospheric aerosols using CE and photometric AWC or isocratic IC (the  $\pm$  values are the confidence limits at the 95% level). Top:  $n = 140$ ; slope =  $0.975 \pm 0.013$ ; intercept =  $0.031 \pm 0.007$ ;  $R^2 = 0.9794$ . Bottom:  $n = 140$ ; slope =  $0.999 \pm 0.011$ ; intercept =  $0.040 \pm 0.006$ ;  $R^2 = 0.9875$ .

mean ratio of the individual results higher than quantitation limit of analyte obtained by the respective technique. Some outlier ratios were rejected. In all instances there was a close agreement between the tested techniques (Table 4). For the sulphate, mean ratios were within range 0.9393–1.0406 when compared to photometric AWC results. The lowest ratio was obtained by the evaluation of isocratic IC and AWC results. The excellent agreement between gradient IC and CE sulphate results was observed. The isocratic IC results were about 10%

lower than gradient IC results. For total nitrate and nitrite as a nitrogen analysis, the better agreement was obtained by CE than IC when compared to AWC technique. Results obtained by gradient IC were about 10% lower.

### 3.3. Operational considerations

#### Analysis time

The number of analyte samples (an analyte is defined as an analysis of a constituent in a

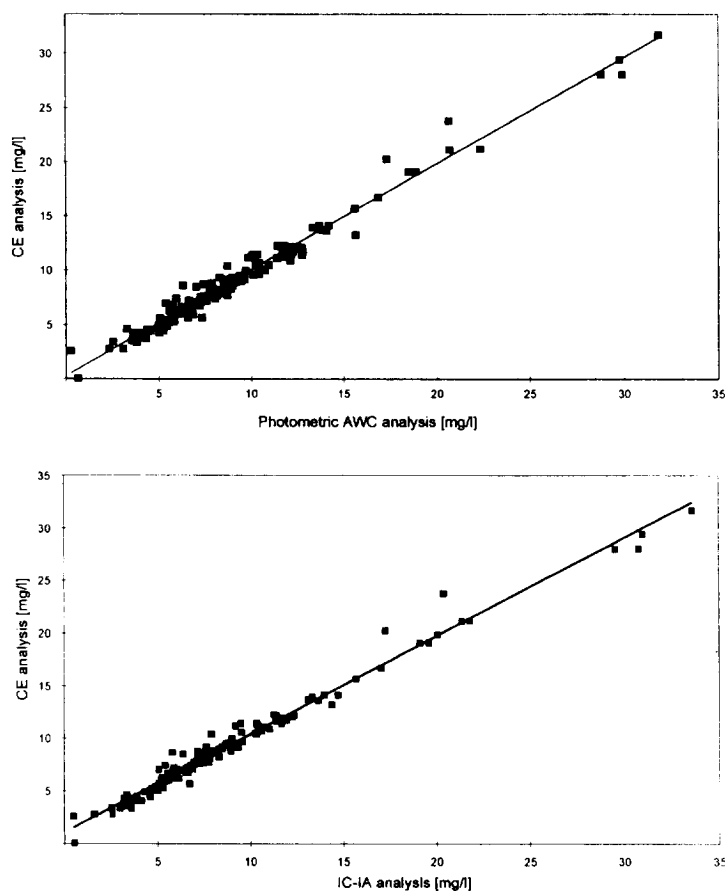


Fig. 3. Comparison of the results for the determination of sulphate in atmospheric aerosols using CE and photometric AWC or isocratic IC (the  $\pm$  values are the confidence limits at the 95% level). Top:  $n = 144$ ; slope =  $0.979 \pm 0.012$ ; intercept =  $0.273 \pm 0.132$ ;  $R^2 = 0.9773$ . Bottom:  $n = 144$ ; slope =  $0.936 \pm 0.011$ ; intercept =  $1.040 \pm 0.113$ ;  $R^2 = 0.9808$ .

standard, a quality control sample or an actual sample) possible to analyze during the working day (AWC) and running overnight (IC and CE) is presented in Table 1. The slowest analysis is performed by the multi-dimensional IC system due to a long anion gradient method (Fig. 1). However, the ability of this system to make simultaneous determination of 14 anions and 11 cations on a single sample is highly advantageous. As a result of this, the number of analytes determined per day by both IC and CE is comparable and larger than the photometric AWC.

#### *Cost of consumables*

Estimation of operational costs due to consumables (chemicals, columns, autosampler vials etc.) based on 2400 samples being run per year was performed. The lowest analyte operational costs were estimated by the use of CE, followed by isocratic IC and photometric AWC.

#### *Waste generation and disposal*

CE wastes are generated in much smaller quantities than photometric AWC and IC wastes. Approximately 60 ml of electrolyte are gener-



Table 3  
Statistical analysis results ( $\pm 95\%$  confidence limit)

Method tested		Method compared	
		Photometric AWC	IC-IA
<i>Nitrate + nitrite (N)</i>			
CE <sup>a</sup>	$R^2$	0.9794	0.9875
	Slope	$0.975 \pm 0.013$	$0.999 \pm 0.01111$
	Intercept	$0.031 \pm 0.007$	$0.040 \pm 0.006$
IC-IA	$R^2$	0.9840	
	Slope	$0.9711 \pm 0.010$	
	Intercept	$-0.007 \pm 0.005$	
IC-GA	$R^2$	0.9816	0.9977
	Slope	$0.941 \pm 0.010$	$0.970 \pm 0.004$
	Intercept	$-0.011 \pm 0.006$	$-0.005 \pm 0.002$
<i>Sulphate</i>			
CE <sup>b</sup>	$R^2$	0.9773	0.9808
	Slope	$0.979 \pm 0.012$	$0.936 \pm 0.011$
	Intercept	$0.273 \pm 0.132$	$1.040 \pm 0.113$
IC-IA	$R^2$	0.9918	
	Slope	$1.043 \pm 0.008$	
	Intercept	$-0.810 \pm 0.083$	
IC-GA	$R^2$	0.9907	0.9974
	Slope	$1.051 \pm 0.008$	$1.007 \pm 0.004$
	Intercept	$-0.081 \pm 0.089$	$-0.742 \pm 0.044$

Total number of samples was 145. All results were blank corrected. IC-IA, IC-GA = Isocratic and gradient IC elution, respectively.

<sup>a,b</sup>5 and 1 outliers were rejected, respectively.

ated per day during which some 100 samples can be analyzed. This much is generated in 6, 120 and 30 min of photometric AWC, single isocratic IC or multi-dimensional IC system, respectively. Also, the photometric AWC wastes are more toxic.

#### 4. Conclusions

When using the equipment and types of samples described in this paper the following were found: (i) sulphate and nitrate analysis by CE correlates well with automated photometric analysis and IC; (ii) both IC and CE offer advantages by performing sensitive simultaneous multi-ion analysis in one assay rather than two

separate assays in photometric AWC; (iii) CE is less expensive to operate and less waste is generated than by IC. Both IC and CE produce less toxic waste than the photometric methods. Drawback of the CE method based on presented analysis is that CE is less sensitive than IC. However, the CE sensitivity is acceptable for the described application. Also CE analyte migration times are more strongly affected by the sample matrix. Because of this effect the use of an internal standard is recommended.

In conclusion, the results suggest that the CE can be applied very advantageously in a routine determination of sulphate, nitrate and other anions in atmospheric aerosols. The CE method may also be useful for comparison of the results when two independent methods are required for control of the quality of analytical work.

Table 4  
Ratio of results

Methods	$n_{\text{tot}}^a$	$n_{\text{out}}^b$	Median	Mean	R.S.D. (%)
<i>Nitrate + nitrite (N)</i>					
CE vs. AWC	94	0	1.0420	1.0437	15.14
CE vs. IC-IA	124	5	1.1271	1.1639	17.06
CE vs. IC-GA	124	5	1.1692	1.2393	22.42
IC-IA vs. AWC	94	0	0.9490	0.9326	13.23
IC-GA vs. AWC	94	0	0.9164	0.8854	16.74
IC-GA vs. IC-IA	141	2	0.9580	0.9560	10.47
<i>Sulphate</i>					
CE vs. AWC	142	1	0.9969	1.0138	9.38
CE vs. IC-IA	145	3	1.0765	1.0862	10.42
CE vs. IC-GA	145	2	0.9563	0.9721	8.10
IC-IA vs. AWC	142	0	0.9367	0.9393	8.06
IC-GA vs. AWC	142	0	1.0427	1.0406	7.88
IC-GA vs. IC-IA	145	0	1.1233	1.1077	4.24

Total number of samples was 145. All results were blank corrected. IC-IA, IC-GA = Isocratic and gradient IC elution, respectively.

<sup>a</sup>Number of samples for which the individual result was higher than quantitation limit.

<sup>b</sup>Number of rejected outliers.

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