



ELSEVIER

Journal of Chromatography A, 671 (1994) 389–395

JOURNAL OF  
CHROMATOGRAPHY A

# Application of capillary electrophoresis in atmospheric aerosols analysis: determination of inorganic and organic anions

Ewa Dabek-Zlotorzynska\*, Joseph F. Dlouhy

*Chemistry Division, Environmental Technology Centre, Environment Canada, 3439 River Road, Ottawa, Ontario K1A 0H3, Canada*

## Abstract

The usefulness of capillary electrophoresis in the analysis of inorganic and organic anions in atmospheric aerosols was investigated. Various electrolytes based on chromate, pyromellitate (PMA), phthalate and 2,6-naphthalenedicarboxylate (NDC) were tested. Two separate electrolyte systems (PMA and NDC) are recommended for determination of anions with different mobility. Results obtained by parallel analysis of sulphate by capillary electrophoresis and ion chromatography in atmospheric aerosols are presented.

## 1. Introduction

The measurement of the chemical composition of atmospheric aerosols has been and still is the subject of many studies using different analytical techniques and collection methods.

For the determination of inorganic anions, ion chromatography (IC) has become the technique of choice [1]. It has already reached a stage of maturity, so that its potential and limitations are by now well known. Other new techniques such as capillary electrophoresis (CE) have only been introduced in the last several years [2–5].

Capillary electrophoresis is revolutionizing separation science. CE and related techniques such as micellar electrokinetic capillary chromatography (MECC) or capillary gel electrophoresis (CGE) offer a high separation efficiency and separation speed for charged and neutral species, and great progress has been made in instrumentation and applications in recent years

[6,7]. Applications include the separation of small inorganic and organic anions with indirect UV detection in many real samples [9–19]. Excellent separation efficiencies were reported with chromate, pyromellitate and other aromatic carboxylic acid salts containing electrolytes [7–21].

This study was undertaken to investigate the usefulness of CE in the analysis of inorganic and organic anions in atmospheric aerosols. Also, this study was performed to obtain independent complementary confirmation of the IC results. CE may be used as a complement to IC analysis [13,16], because the selectivity for anion separation by CE differs significantly from that obtained using anion exchange columns in IC. In order to obtain the best selectivity of CE separation, and sensitivity with indirect detection, various potential electrolytes such as chromate [8], pyromellitate (PMA) [20], phthalate [11] and 2,6-naphthalenedicarboxylate (NDC) [21] were investigated. This paper presents also results obtained by parallel analysis of sulphate in the

\* Corresponding author.

aqueous atmospheric aerosol extracts by CE and IC methods.

## 2. Experimental

### 2.1. Capillary electrophoresis

All CE experiments were performed with a Beckman P/ACE 2100 instrument (Fullerton, CA, USA) equipped with a multi-wavelength UV detector, an automatic sample changer, a liquid thermostated capillary cartridge (capillary 75  $\mu\text{m}$  I.D.  $\times$  375  $\mu\text{m}$  O.D.  $\times$  57 cm total length, 50 cm to detector) and an IBM PS/2 70 personal computer utilizing Beckman Gold System (V 7.11) software for instrument control and data collection.

Prior to use the capillary was pretreated with 0.1 M NaOH for 10 min, then rinsed with deionized water and the used electrolyte. To maintain good peak shapes and reproducible migration times, the capillary tube was rinsed with the running electrolyte for 1 min before the sample was injected. The capillary temperature was kept at  $25 \pm 0.1^\circ\text{C}$  by means of a fluoro-carbon liquid continuously circulating through the cartridge. Unless otherwise noted, all in-

jections were achieved using a 10-s pressure injection technique.

All electrolyte compositions and operating conditions used in this study are presented in Table 1. The electrolytes were filtered and degassed by creating a vacuum inside the syringe.

### 2.2. Ion chromatography

The IC system used in this study was from Dionex (Sunnyvale, CA, USA) as described previously [22]. Separation of anions by gradient elution was performed on an IonPac-AS10 column with an IonPac-AG10 guard column. Conductivity detection was carried out using an anion self-regenerating suppressor (ASRS-1) in the recycle mode.

### 2.3. Reagents

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

All chemicals were purchased commercially from either Aldrich (Milwaukee, WI, USA) or Fisher Scientific (Ottawa, ON, Canada) in the highest purity available, and were used as is

Table 1  
Experimental conditions for CE analysis

Conditions	Chromate (E1)	PMA <sup>a</sup> (E2)	Phthalate (E3)	NDC <sup>b</sup> (E4)
Electrolyte composition	5.0 mM chromate 0.5 mM TTAB <sup>d</sup> pH = 8.0	2.25 mM PMA 0.75 mM HMOH <sup>e</sup> 6.50 mM NaOH 1.60 mM TEA <sup>f</sup> pH = 7.7	5.0 mM KHP <sup>c</sup> 0.5 mM TTAB 1.0 mM boric acid pH = 5.9	2.0 mM NDC 0.5 mM TTAB 5.0 mM NaOH pH = 10.9
Polarity	(-)	(-)	(-)	(-)
Detection	Indirect, 254 nm	Indirect, 254 nm	Indirect, 254 nm	Indirect, 280 nm
Voltage	20 kV	30 kV	20 kV	20 kV
Injection	Pressure, 10 s	Pressure, 10 s	Pressure, 10 s	Pressure, 10 s

<sup>a</sup> Pyromellitic acid

<sup>b</sup> 2,6-Naphthalenedicarboxylic acid

<sup>c</sup> Potassium hydrogen phthalate

<sup>d</sup> Tetradecyltrimethylammonium bromide

<sup>e</sup> Hexamethonium hydroxide

<sup>f</sup> Triethanolamine

without further purification. Pyromellitate based electrolyte was obtained from Dionex.

#### 2.4. Quantitation procedure

The CE procedures were calibrated with freshly prepared mixed standard solutions every day that samples were analyzed. The mixed anion stock solution was diluted to produce working standard solutions at four different concentrations within the range 0.2–10  $\mu\text{g/ml}$ . Calibration graphs were plotted based on the linear regression analysis of the corrected peak area (peak area/migration time).

Identification of individual ions was based on the comparison of migration times of analytes with those of standard solutions. Some samples were spiked with standard solution. Ion chromatography results were also used for identification of some ions.

Detection limits were defined as three times the standard deviation of 18 replicate analyses of the standard with concentration about ten times the expected detection limit.

#### 2.5. Filter extraction

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

PTFE filter collected aerosols were non-destructively analyzed by X-ray fluorescence (XRF) for fifty elements. Then, the chemical analysis of extracts of atmospheric aerosols was performed using ion chromatography [22] and capillary electrophoresis. The extraction of water soluble aerosols collected on filters was performed with 15 ml of water by sonication in an ultrasonic bath (Branson and Smithkline, Model Bransonic 42) for 30 min. Before addition of water, the filters with collected aerosols were wetted with 100  $\mu\text{l}$  of isopropanol. The extracts were analyzed less than 24 h after extraction.

The residue of extracts was preserved by storage at  $-20^\circ\text{C}$  [23].

### 3. Results and discussion

#### 3.1. Selection of electrolyte

One of the major aims of this work was to investigate the utility of various potential electrolytes for the determination of inorganic and organic anions in atmospheric aerosols. In this work, four electrolytes with different mobilities and with strong UV absorption were investigated.

Fig. 1 shows the four electropherograms obtained with the 14-anion mixture with tested electrolytes under conditions listed in Table 1. The chromate electrolyte shows most of the tested anions fully resolved with increasing tailing for the later peaks. Under conditions proposed by Harold *et al.* [20], the PMA electrolyte shows better resolution of bromide (Peak 1) through to oxalate (Peak 6) in comparison to the chromate electrolyte separation. However, other less mobile anions are separated at times longer than 5 min. The phthalate and NDC electrolyte separations show improved peak symmetry for less mobile anions, but fail to resolve inorganic anions.

Sensitivities of the tested methods expressed as the response (corrected peak area) per unit concentration (slope of the calibration curve) were compared. The ratio of sensitivities for the PMA, phthalate and NDC methods *vs.* the chromate method is presented in Table 2. As can be seen, a better sensitivity for inorganic anions is obtained using the PMA than the chromate based electrolyte. The NDC electrolyte shows the best sensitivity and selectivity for less mobile anions (formate through benzoate).

Table 3 summarizes the migration time and peak area precision (R.S.D.) for tested anions in a mixed standard under conditions listed in Table 1. Excellent precision of migration times was observed with the PMA and NDC based electrolytes. Precision of peak areas was better

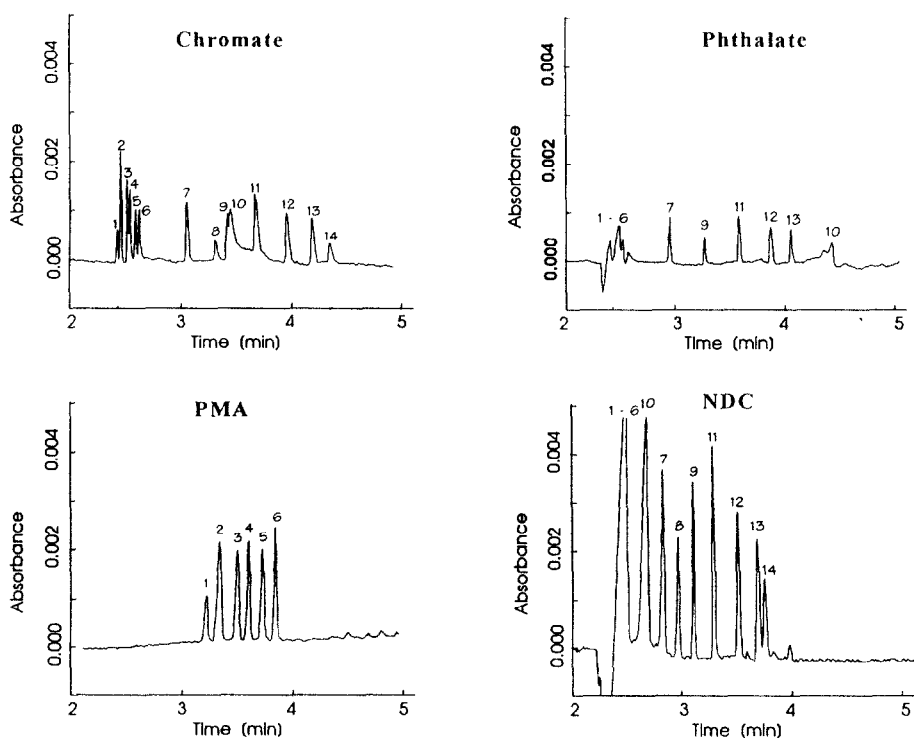


Fig. 1. Electropherograms of a 4 µg/ml anion mixed standard obtained with tested electrolyte compositions. Peaks: 1 = bromide; 2 = chloride; 3 = sulphate; 4 = nitrite; 5 = nitrate; 6 = oxalate; 7 = formate; 8 = phthalate; 9 = methanesulphonate; 10 = bicarbonate or carbonate; 11 = acetate; 12 = propionate; 13 = butyrate; 14 = benzoate. See Table 1 for more details.

Table 2  
Sensitivity ratio and detection limit

Ion	Sensitivity ratio			Detection limit (ng/ml)	
	E2/E1	E3/E1	E4/E1	E2	E4 [21]
Bromide	1.72	—	—	210	—
Chloride	1.50	—	—	188	—
Sulphate	1.30	—	—	168	—
Nitrite	1.41	—	—	220	—
Nitrate	1.77	—	—	219	—
Oxalate	1.57	—	—	190	—
Formate	1.33	0.42	3.15	166	133
Acetate	—	0.52	2.14	—	102
Propionate	—	0.55	2.60	—	102
Butyrate	—	0.58	2.28	—	118

E1, E2, E3, and E4 are the chromate, PMA, phthalate and NDC based electrolytes, respectively. For more details see Table 1

Table 3  
Comparison of precision

Ion	Relative standard deviation (%) <sup>a</sup>					
	Migration time			Peak area		
	Chromate	PMA	NDC [21]	Chromate	PMA	NDC [21]
Bromide	0.74	0.19	–	8.80	6.17	–
Chloride	0.64	0.19	–	4.68	4.09	–
Sulphate	0.66	0.22	–	3.41	3.99	–
Nitrite	0.67	0.21	–	3.95	3.65	–
Nitrate	0.68	0.23	–	3.92	4.98	–
Oxalate	0.66	0.28	–	3.09	5.43	–
Formate	1.20	0.29	0.32	4.73	3.11	4.43
Acetate	1.27	–	0.38	5.46	–	3.42
Propionate	1.39	–	0.45	6.09	–	3.39
Butyrate	1.43	–	0.48	8.29	–	3.94

<sup>a</sup> Relative standard deviation from 18 replicates of anion mixed standard at concentration 4 µg/ml.

than 5% for most of the anions under investigation.

These results show that with respect to the separation ability and sensitivity, the use of two separate electrolyte systems is preferable. Major inorganic anions in aqueous extracts of coarse and fine atmospheric aerosols were determined using the PMA based electrolyte. Separation of aliphatic carboxylic acids and other organic compounds was performed with the NDC based electrolyte.

Detection limits (for a 10-s pressure injection) of anions studied with the PMA and NDC based

electrolytes are listed in Table 2. It can be seen that all anions have detection limits in the ng/ml range.

### 3.2. Determination of anions in atmospheric aerosols

Typical electropherograms of coarse and fine atmospheric aerosol extracts are presented in Fig. 2. Coarse atmospheric aerosol particles contain chloride, sulphate and nitrate as the major ions, as reported previously [22]. Sulphate is the major ion of fine atmospheric aerosols.

Table 4  
Recovery data of quality control sample

Ion	Recovery Inter-laboratory median [24] (µg/ml)	Mean (%)						
		CE			IC			
		iso		gra	CE		IC	
		iso	gra	iso	gra			
Chloride	2.135	99.79	98.85	102.92	4.38	3.19	1.41	
Sulphate	8.811	104.55	99.75	107.16	1.89	2.11	1.65	
Nitrate	5.301	104.13	100.70	101.32	2.21	2.59	2.16	

Reported results are the mean and relative standard deviation of 14 (CE) and 4 (IC) replicates. Iso and gra are isocratic and gradient elution, respectively.

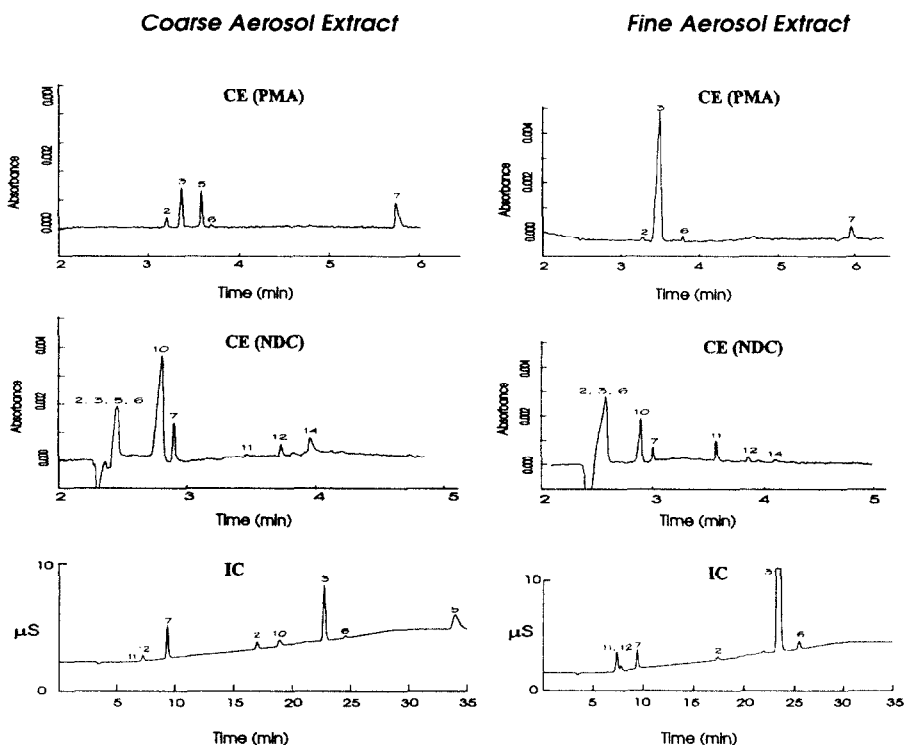


Fig. 2. Analysis of coarse and fine atmospheric aerosol extracts using CE and IC methods. A 30-s injection time was used with the PMA based electrolyte; see Table 1 for more details. Peaks are the same as in Fig. 1.

Organic anions such as formate and acetate are also present in atmospheric aerosols.

Results obtained by parallel analysis of sulphate in the extracts of atmospheric aerosols by CE and IC methods were compared. To date nearly 90 filter samples have been analyzed. Only sulphate was present in a sufficient amount to allow a quantitative comparison of results obtained by the two independent separation methods. Fig. 3 shows a high degree of correlation between CE and IC results for sulphate (CE = 0.91 IC (gradient) + 0.19,  $r^2 = 0.9953$ ; CE = 1.03 IC (isocratic) + 0.03,  $r^2 = 0.9969$ ). Some outliers are present. Additional studies are needed to explain these differences in measured sulphate concentrations between the two methods.

To evaluate the accuracy of CE and IC results, an external control sample was analyzed in the same manner as the samples. The recovery data

for the external quality control sample presented in Table 4 agree with interlaboratory medians [24]. The analytical results are also precise as shown by the standard deviation.

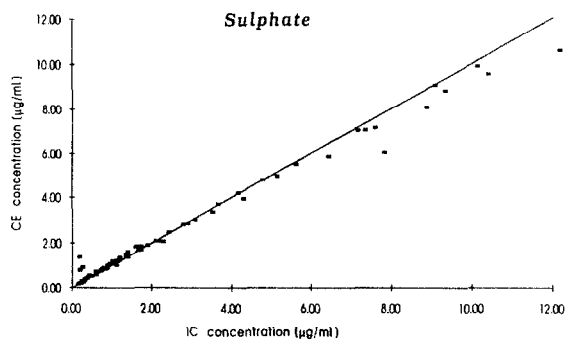


Fig. 3. Comparison of sulphate determined by CE (PMA electrolyte) vs. the gradient IC method. The solid line indicates the 1:1 relationship between CE and IC results.

#### 4. Conclusions

Results of this work show that capillary electrophoresis is an effective separation method for the determination of anions in atmospheric aerosols. This technique provides highly efficient separation with high accuracy, precision, short analysis time and low reagent consumption. However, two separate electrolyte systems (PMA and NDC) are recommended for analysis of inorganic and organic anions.

Capillary electrophoresis also complements ion chromatography, the recognized method of ion analysis, and thus greatly reduces problems caused by interfering ions and allows easy peak confirmation. Work continues in this laboratory towards the adoption of CE to other types of samples of interest.

#### 5. References

- [1] P.R. Haddad and P.E. Jackson, *Ion Chromatography: Principles and Applications (Journal of Chromatography Library, Vol. 46)*, Elsevier, Amsterdam, 1990.
- [2] F. Mikkers, F. Everaerts and T. Verheggen, *J. Chromatogr.*, 169 (1979) 1–10.
- [3] F. Mikkers, F. Everaerts and T. Verheggen, *J. Chromatogr.*, 169 (1979) 11–20.
- [4] J.W. Jorgenson and K.D. Lukacs, *J. Chromatogr.*, 218 (1981) 209–261.
- [5] J.W. Jorgenson and K.D. Lukacs, *Anal. Chem.*, 53 (1981) 1298–1302.
- [6] W.G. Kuhr, *Anal. Chem.*, 62 (1990) 403R–414R.
- [7] P. Jandik and G. Bonn, *Capillary Electrophoresis of Small Molecules and Ions*, VCH Publishers: New York, 1993.
- [8] W.R. Jones and P. Jandik, *Amer. Lab.*, 22(9) (1990) 51.
- [9] W.R. Jones and P. Jandik, *J. Chromatogr.*, 546 (1991) 431–443.
- [10] W.R. Jones and P. Jandik, *J. Chromatogr.*, 546 (1991) 445–458.
- [11] B.F. Kenney, *J. Chromatogr.*, 546 (1991) 423–430.
- [12] B.J. Wildman, P.E. Jackson, W.R. Jones and P.G. Alden, *J. Chromatogr.*, 546 (1991) 459–466.
- [13] J. Romano, P. Jandik, W.R. Jones and P.E. Jackson, *J. Chromatogr.*, 546 (1991) 411–421.
- [14] G. Bondoux, P. Jandik and W.R. Jones, *J. Chromatogr.*, 602 (1992) 79–88.
- [15] D.R. Salmon and J. Romano, *J. Chromatogr.*, 602 (1992) 219–225.
- [16] K.A. Hargadon and B.R. McCord, *J. Chromatogr.*, 602 (1992) 241–247.
- [17] S.C. Grocott, L.P. Jefferies, T. Bowser, J. Carnevale and P.E. Jackson, *J. Chromatogr.*, 602 (1992) 257–264.
- [18] J.P. Romano and J. Krol, *J. Chromatogr.*, 640 (1993) 403–412.
- [19] J.B. Nair and C.G. Izzo, *J. Chromatogr.*, 640 (1993) 445–463.
- [20] M.P. Harold, M.J. Wojtusik, J. Rivello and P. Henson, *J. Chromatogr.*, 640 (1993) 463.
- [21] E. Dabek-Zlotorzynska and J.F. Dlouhy, *J. Chromatogr.*, submitted for publication.
- [22] E. Dabek-Zlotorzynska and J.F. Dlouhy, *J. Chromatogr.*, 640 (1993) 217–226.
- [23] E. Dabek-Zlotorzynska, D. Mathieu and J.F. Dlouhy, *The Stability of Aqueous Extracts of Aerosols. Ion Chromatographic Determination of the Effects of Some Preservation Methods*, Environmental Technology Centre, Environment Canada, Ottawa, ON, Canada, 1993.
- [24] N. Arafat and K.I. Aspila, *LRTAP Intercomparison Study L-33; Major Ions, Nutrients and Physical Properties in Water*, National Water Research Institute, Burlington, ON, Canada, 1993.