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Determination of low-molecular-mass carboxylic acids in atmospheric aerosol and vehicle emission samples by capillary electrophoresis

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Abstract

A method is developed for the determination of a large number of airborne and vehicle-emitted low-molecular-mass mono- and dicarboxylic acids using capillary electrophoresis with indirect UV detection. A background electrolyte (BGE) consisting of 2,6-naphthalenedicarboxylic acid and tetradecylmethylammonium bromide, adjusted to pH 6.2 with 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol, is employed. Separations are robust using the buffered BGE, proper rinse steps, and constant current mode with migration time variations less than 3% RSD on a day-to-day basis, using different capillaries and performed by different analysts. Detection limits are at the tens of μg/l level using pressure injection. A comparison of the CE method with ion chromatography is also made. © 2001 Published by Elsevier Science B.V.

Keywords: Air analysis; Aerosols; Carboxylic acid

1. Introduction

During the last decade, many reports have been published on the importance of monitoring airborne carbonaceous pollutants including low-molecular-mass (low-M_r) carboxylic acids. These acids are found in a wide variety of marine and continental environments, such as urban, rural and remote atmospheres [1–6]. Numerous studies have shown that carboxylic acids contribute significantly to ambient and precipitation acidity [7,8]. There is much agreement that the primary sources of carboxylic acids in the atmosphere comprise both anthropogenic and biogenic emissions, in addition to photochemical transformations of precursors in aqueous, gaseous and particulate phases [1]. The influx of carboxylic acids to the urban atmosphere has been associated with vehicle emission as well as with other anthropogenic sources [9,10]. Similarly, low-M_r carboxylic acids have direct and indirect emission sources in the nonurban atmosphere, such as forest fires and photochemical oxidation of biogenic hydrocarbons [11]. Determination of the sources and types of organic acids, in addition to the inorganic acid species more commonly measured, is of great importance for a

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complete understanding of the nature of acidity of ambient aerosols. It is relevant to a number of important atmospheric chemistry issues including air quality, acid precipitation and health effects of particulate matter.

Various analytical techniques have been employed to measure airborne and vehicle-emitted carboxylic acids, as recently reviewed [12]. The current analytical techniques for the determination of such analytes are usually based on chromatographic methods including gas chromatography (GC), high-performance liquid chromatography (HPLC) and ion chromatography (IC). However, there is still a demand for techniques that avoid time-consuming derivatization often necessary in GC, or overcome insufficient separation efficiency and selectivity sometimes encountered in HPLC and IC [12–14].

More recently, capillary electrophoresis (CE) has been developed into a powerful analytical technique with a broad environmental application potential as shown in recent reviews [15–17]. Thanks to its high efficiency, speed and economy of analysis, it is becoming recognized as a potential complement to the currently used GC and IC techniques. Significant progress has been made in CE methodologies to assure precise quantitative results [18–23], but the widespread use of CE as a routine quantitative tool for environmental analysis is still limited. This observation can be explained by the reluctance of analysts to adopt new technology or by the wide ubiquity of GC and IC.

CE with direct or indirect UV detection has been used to determine low-M_r carboxylic acids in various matrices [12,24,25]. Nevertheless, the sensitivity for direct UV detection is low for weak UV absorbance of carboxylic acids. Thus, most CE separations of low-M_r carboxylic acids are using indirect UV detections. These works include the study of different electrolyte compositions to achieve the best separation efficiency, sensitivity and speed. Several reports have also described the development and application of CE with indirect UV detection for the determination of airborne and vehicle-emitted low-M_r carboxylic acids [5,14,20,26–30]. For example, Souza et al. [5] used CE to confirm the IC identification of some diurnal and nocturnal atmospheric gas- and particle-phase carboxylic acids collected in Sao Paulo, Brazil. CE has been also shown as a versatile analytical technique for the study of vehicular emission [28].

Our objective was to develop a CE method for analysis of a larger number of aliphatic mono-, hydroxy-, keto- and dicarboxylic acids as well as aromatic acids found in the atmosphere and vehicle emissions. In this study, a previously developed CE method using 2,6-naphthalenedicarboxylate-based background electrolyte (BGE) for indirect UV detection [27] has been modified and expanded to allow measurement of oxalate and several other mono- and dicarboxylic acids. The work has been focused on the optimization of electrolyte composition, capillary conditioning procedure, and separation mode. The new developed method is rapid, sensitive and quantitative and can be readily applied to atmospheric aerosol and vehicle emission samples for the determination of these analytes. A comparison of the CE method with IC is also made.

2. Experimental

2.1. Apparatus

All CE experiments were performed on a Beckman P/ACE 2100 CE instrument (Fullerton, CA, USA), using its System Gold software for data acquisition and processing. Polymicro (Phoenix, AZ, USA) capillaries with an inner diameter of 75 μm, an outer diameter of 365 μm and a total length of 57 cm (50 cm to the detector) were used. Unless otherwise stated, capillary cartridges with a 100× 200 μm aperture were used. The capillary temperature was controlled at 25.0±0.1°C by means of a fluorocarbon liquid being continuously circulated through the cartridge. Peaks were detected at 214 nm with a bandwidth of 10 nm, using a response time of 0.2 s and a data acquisition rate of 10 Hz.

IC analyses were performed on a Dionex DX 300 system (Sunnyvale, CA, USA) equipped with an advanced gradient pump (Model AGP), an ASRS-Ultra anion self-regenerating suppressor, a conductivity detector (CDM-II), an automated sampler with 5-ml vials and a Rheodyne injection valve with 25-μl sample loop. Separation of low-M_r carboxylic acids was performed on a Dionex IonPacAS11 column (250 mm×2 mm I.D.) with an IonPacAG11

guard column (50 mm×2 mm I.D.) using NaOH gradient elution under conditions recommended by the manufacturer [31]. An anion trap column (ATC) was used in order to minimize the baseline shift caused by carbonate and other anionic contaminant levels in the eluent. System control as well as data acquisition and processing were carried out by Dionex AI-450 chromatography software.

2.2. Reagents and standards

Chemicals used in this work were of the highest purity available and used without further purification. The low-M_r carboxylic acids (either as the free acids or as their sodium salts), 2,6-naphthalenedicarboxylic acid (NDC) and tetradecylmethylammonium bromide (TTAB) were purchased from Aldrich (Milwaukee, WI, USA). 2,2-Bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (Bis-Tris) was obtained from ICN Biochemicals (Aurora, OH, USA). All other chemicals were purchased from Fisher Scientific (Ottawa, Canada).

All solutions were prepared using deionized water (18 MΩ cm). Stock solutions of carboxylic and other acids used (1000 mg/l) were prepared by dissolving appropriate amount of acids or their sodium salts in degassed water. The mixed standards were obtained by appropriate dilution of stock solutions and stored at 4°C. All diluted standards were prepared daily from the stock standard solutions.

2.3. Preparation of background electrolyte

All BGE solutions containing 4 m*M* NDC–14.4 m*M* Bis-Tris–0.2 m*M* TTAB at pH 6.2 were prepared by dissolving an appropriate amount of NDC in a certain volume of Bis-Tris solution (100 m*M*) and water, sonicating for about 20 min until all NDC was dissolved, and adding an appropriate volume of TTAB solution (10 m*M*). Note that due to limited solubility of NDC in water, NDC was first wetted with methanol (100 μl) before addition of water. Finally, the solution was transferred quantitatively to a volumetric flask and diluted with water to the graduated marker. No adjustment of the pH was necessary to keep pH 6.2. The resulting mixture was then filtered through a 0.45-μm PTFE filter (Gelman Science, Montreal, Canada). In a routine operation, it was important to use at least weekly prepared NDC buffer at the start of each series of analyses.

2.4. Capillary treatment and procedures

Prior to first use, a new capillary was rinsed with methanol (10 min), deionized water (1 min), 0.5 *M* NaOH (10 min), deionized water (10 min) and finally BGE solution (20 min). As a daily routine procedure, the capillary was conditioned by flushing with 0.1 *M* NaOH (10 min), deionized water (2 min) and finally BGE solution (20 min), followed by application of −15 kV (15 min). At the end of the day, the capillary was rinsed with 0.1 *M* NaOH (5 min) and deionized water (5 min), followed by flushing with air (2 min). In between injections, the capillary was flushed with 0.1 *M* NaOH (1 min), then dipped in water vials, and rinsed with BGE solution (2 min). These conditioning and flushing procedures for the capillary were essential to obtain reproducible results.

The CE operating conditions were varied according to the experiments. Unless otherwise stated, sample injection was carried out either by pressure (0.5 p.s.i., 10 s; 1 p.s.i.=6894.76 Pa) or by electrokinetic (10 kV, 10 s).

In constant voltage mode, the separation voltage was −15 kV. As a reversed electroosmotic flow (EOF) was required, the high-voltage power supply was operated in negative mode. In constant current mode, 6.6±0.2 μA was applied. Different vials of BGE (4 ml) were used for rinsing and electrophoresis in order to keep the electrolyte level constant on the inlet side. Two vials of water were used for dipping the capillary ends to avoid cross-contamination.

Detection limits were determined by analyzing dilute solutions. They were taken from at least seven replicate analyses of a sample containing analytes each at a concentration about 10 times higher than the estimated detection limit (or the concentration giving a signal-to-noise ratio of 3). The detection limits were calculated at the 95% confidence level ($DL=t_{n-1}s$, where "t" is the Student coefficient, "n" is the number of replicates and "s" is the standard deviation).

Quantitative results were obtained using corrected peak area (CPA) which was the peak area normalized

with respect to the migration time (peak area/migration time).

2.5. Samples and sample preparation

Aerosol fine particles (aerodynamic diameter<2.5 μm), collected on 47-mm PTFE filters using a Partisol air sampler at a flow-rate of 16.7 l/min for 24 h, were obtained from the Ambient Measurement Section of Analysis and Air Quality Division, Environmental Technology Centre, Environment Canada.

KOH-coated quartz fiber filters were used to collect gaseous low-M_r carboxylic acids in vehicle emissions. They were obtained from the Emission Research and Measurement Division of Environmental Technology Centre, Environment Canada, as a part of the Program for Energy Research and Development project. A PTFE membrane filter was used upstream of the KOH filter to remove particulate matter. The vehicle emission or dilution air was sampled at a constant flow-rate of 16.7 l/min for 23 min. The gas stream sampled in both cases was at room temperature.

The samples including blank filters were extracted with 10 ml of deionized water in an ultrasonic batch (Branson and SmithKline, Model Bransonic 42) for 30 min. All extracts were passed through a Dionex OnGuard-H cartridge containing strong acid resin in the H^+ form. The use of this sample treatment method was found to be indispensable for removing the high levels of K^+ ions and converting the high concentration of hydroxide ions to water; otherwise, both CE and IC analyses could not be performed due to matrix interferences. All extracts were analyzed by CE and IC methods as soon as possible after the extraction.

3. Results and discussion

3.1. Optimization of separation conditions and system performance

In a previous paper we reported the CE separation of a variety of organic acids and alkylsulfonates using an unbuffered electrolyte system consisting of 2 m*M* NDC, 5 m*M* NaOH and 0.5 m*M* TTAB at pH 8 or 11 [27]. NDC had been described as a very suitable and sensitive carrier electrolyte for analytes with moderate mobilities such as low-M_r carboxylic acids. TTAB was added to the electrolyte in order to reverse the EOF allowing a short analysis time. However, with this electrolyte composition, analysis of a variety of aliphatic mono-, hydroxy-, keto-, and dicarboxylic acids and aromatic acids that are identified in gas phase and particulate phase of atmospheric and vehicle samples was not possible.

In our search for a better BGE system and separation conditions, two factors were important. First, optimum conditions must be selected in order to separate a variety of low-M_r carboxylic acids identified in atmospheric aerosol and vehicle emission samples. Second, conditions must be chosen to minimize differences in migration time and peak area from run-to-run, hence achieving reproducible CE results. From this point of view, several parameters were carefully studied in order to modify and improve the previous CE method through changes in the BGE (concentration and pH) and using various buffering agents. In addition, the effects of different control modes, capillary conditioning procedures and injection conditions on precision were investigated. To establish the optimum conditions for CE separation of a variety of low-M_r acids, an aqueous model solution of 12 mono- and dicarboxylic acids was used at a concentration of 2 μg/ml each. Then resolution, detection sensitivity and total time of analysis were chosen as response variables. Optimal conditions were defined as having the highest possible resolution, highest sensitivity and shortest analysis time.

3.1.1. BGE composition

From our previous work [27] and those reported by others [32,33], it was found that the pH, the concentration of the BGE and EOF modifier, and the separation voltage are factors affecting the CE separation of small anions with indirect UV detection. Therefore, the present optimization of separation conditions was based on the same factors.

Since the analytes of interest are weak acids with pK_a values below 6, improved resolution was obtained when the pH of the BGE was lowered to 6.2. This agrees with the general rule that better resolution can be obtained when the separation is

performed around the pK_a values of the analytes [34]. Note that below pH 6, the solubility of NDC becomes more problematic. The resolution of malonate and formate was found to decrease with decreasing pH whereas resolution between formate and malate increased (data not shown). As expected, increasing the NDC concentration and decreasing the TTAB concentration resulted in better resolution of the tested acids (data not shown). However, the increase of the NDC concentration leads to the decrease in sensitivity (S/N). For example, detection sensitivity with 4 m*M* NDC in BGE was higher by about 25% than that with 5 m*M* NDC. As sensitivity is an important issue for atmospheric aerosol analysis, the optimum concentration of 4 m*M* of NDC was chosen. It is a compromise between sensitivity and resolution.

Subsequent experiments were carried out to select a BGE composition that yielded a good buffering capacity. Since small differences in pH can cause changes in the selectivity and deteriorations of both resolution and run-to-run repeatability [35], control of buffer ion depletion due to electrolysis of the BGE is one of the key factors in obtaining reproducible CE results [36]. It is well known, that buffering of the BGE has a crucial influence on pH changes and thus effect on CE performance [37–40]. Clearly, it is important to use electrolytes of sufficient buffering capacity to avoid detrimental migration time drifts due to buffer depletion. Bis-Tris was chosen as the buffering reagent in the BGE since the pH 6.2 chosen is closely matched to the pK_a of this counterion (pK_a=6.5). Further studies also showed that due to its high buffering capacity it was possible to carry out daily runs without changing the electrolyte. Also, its very low conductivity avoided the occurrence of distributing Joule heating effects.

Thus, a 4 m*M* NDC–0.2 m*M* TTAB solution adjusted to pH 6.2 using Bis-Tris (14.4 m*M*) was found to be a good compromise between resolution and sensitivity and was used in further experiments.

3.1.2. Effect of washing steps

Fluctuation in the migration times of solutes is one of the major reasons for the lack of precision in CE, which represents a problem in developing routine CE methods. This is particularly important when using non-selective detection, such as an UV–visible absorbance detector, where the identification of an analyte is generally based on its measured migration time and non-reproducible migration time makes this an unsuitable identification parameter. The major cause of non-reproducible migration times is changes in EOF due to unstable surface conditions of the fused-silica wall or small variations in buffer pH. Thus, washing and reequilibration of the inner capillary surface before and during analysis is an important part of quantitative analyses [20,23]. In a recent study, Faller and Engelhardt [23] reported that the proper selection of rinse steps is especially important in CE systems with reversed EOF. It has been demonstrated that even structurally very similar EOF modifiers require totally different combinations of rinse steps. Thus, the development of specific rinse procedures is recommended.

In order to achieve the best migration time repeatability, we studied the effect of different procedures for (i) new capillary conditioning; (ii) capillary washing before and after daily experiments, and (iii) capillary rinsing between runs. Preliminary studies showed that using methanol in addition to NaOH and BGE as rinsing solutions to activate a new capillary resulted in a more stable baseline and more reproducible results. Additionally, when an electroconditioning step (15 min, −15 kV) was applied, a further increase in the precision of migration times was observed, especially at the beginning of each daily analysis. The electroconditioning step caused a faster regeneration of the inner surface, as a consequence, a stable EOF [23]. It was also found that better migration time precision and baseline stability were obtained when the capillary was dried at the end of each day.

Different combinations of rinse steps between runs were tested in the subsequent experiments. The standard rinsing procedure applied in most CE methods is flushing the capillary for several minutes with the running BGE before each sample analysis [20,27,41]. Other procedures such as combinations of NaOH and BGE or HCl and BGE were also described [23]. As can be seen in Fig. 1, using a rinsing procedure with the BGE for 1 min, a poor precision with the RSDs ranging between 0.5% and 0.7% was obtained. Precision of migration times was improved to below 0.3% when the capillary was rinsed with 0.1 *M* NaOH (1 min) followed by BGE

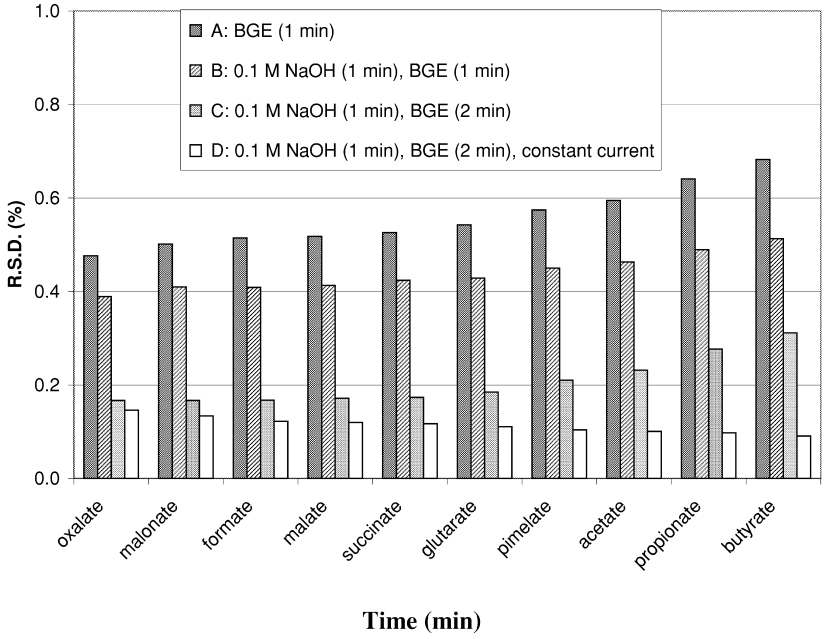

Fig. 1. RSD values of migration times for different rinse steps and run modes. BGE: 4 m*M* NDC–14.5 m*M* Bis-Tris–0.2 m*M* TTAB (pH 6.2); injection: pressure for 10 s; separation mode: (A–C) constant voltage, −15 kV, (D) constant current at 6.6 μA for 7 min, then constant voltage at −15 kV; detection: indirect UV at 214 nm.

(2 min) between runs. Thus, this procedure was used in the following experiments.

3.1.3. Effect of run mode

Significant shift of the migration time with concentration changes of the sample under constant voltage conditions was observed even if all experimental conditions were well controlled. This change in migration time was due to differences in the conductivity of samples containing the analyte ions at different concentrations. In order to reduce such shift, applying constant current instead of constant voltage in the first part of CE separation has been recommended [20,42]. Thus, in subsequent experiments, migration time shifts were evaluated by injecting the model standard at two concentrations (0.4 and 4 mg/l) and varying the duration of constant current application at the beginning of the separation. The magnitude of the current was approximately the same as that under the constant voltage mode. The obtained results showed that dispersion of migration times was significant when a constant voltage was used. The difference in migration time values between the low (0.4 mg/l) and high (4 mg/l) standard concentrations could range in the order of almost 30 s. This excludes the use of an automated external standard calibration system with constant voltage application. The difference in migration times was significantly reduced when a constant current was applied, even for only 1 min. The best results were obtained when the duration of constant current application was at least 5 min. In this case the difference in migration times was found to be one fifth of that obtained at constant voltage. The use of the current mode in the first several minutes of each analysis run after a rinsing process with 0.1 *M* NaOH (1 min) followed by BGE (2 min) resulted in very low RSDs of the migration times, typically better than 0.2% (Fig. 1). Therefore, in further experiments a constant current application for the first 7 min followed by constant voltage application (−15 kV) was used.

3.2. Validation of selected electrophoretic procedure

The final optimized conditions are summarized in the legend of Table 1, with the other conditions (rinse protocol, detector bandwidth, response time and collection time) as specified in the Experimental section. The developed method was then assessed in terms of selectivity, precision, linearity, sensitivity and accuracy for the low-M_r acids of interest. Limits of detection were subsequently determined.

3.2.1. Selectivity

In the analysis of real samples, it is always necessary to investigate the effect of common ions that may be present. Fig. 2 shows a typical electropherogram of a variety of low-M_r organic acids in addition to major inorganic anions commonly present in samples of interest. The separation efficiency was excellent, with minimal overlaps except for pyruvate (peak 17) and suberate (peak 18), as well as benzoate (peak 29) and butyrate (peak 28). As expected, inorganic anions (peaks 1–4) could not be separated with this BGE system as they co-migrated before the organic acids. In addition, under these conditions carbonate–hydrogencarbonate, usually present in environmental samples, did not interfere because the pH of the BGE was lower than the pK_{a1} of carbonate (pK_{a1}=6.35). Also, fluoride was not observed probably due to reaction with the inner wall of the capillary at this pH [43].

As expected, the migration order for the analytes was significantly different from that observed by anion-exchange IC using the IonPac AS11 column. The IonPac AS11 is a low-capacity hydroxide-selective anion-exchange column that provides simultaneous analysis of inorganic and organic anions using sodium hydroxide gradient elution [31]. As can be seen in Fig. 3 all inorganic ions were well resolved. However, several organic acids of interest could not be separated: lactate (peak 25) and fluoride (peak 30); glycolate (peak 19) and acetate (peak 20); butyrate (peak 28) and formate (peak 9); glutarate (peak 12) and adipate (peak 15); malate (peak 10) and succinate (peak 11) and pimelate (peak 16); malonate (peak 7) and carbonate; fumarate (peak 8)

Table 1
Precision of migration times and corrected peak areas (CPAs) on different days with three different capillaries (n=9 each day)[a]

Capillary	Day	Oxalate		Malonate		Formate		Succinate		Acetate		Propionate	
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
Migration time (min)													
1	A	4.50	0.09	5.15	0.09	5.41	0.08	5.70	0.08	7.04	0.10	7.91	0.11
1	B	4.37	0.15	4.98	0.13	5.21	0.12	5.48	0.12	6.69	0.10	7.43	0.10
2	A	4.47	0.24	5.16	0.21	5.40	0.23	6.29	0.21	7.06	0.21	7.91	0.21
2	B	4.43	0.18	5.07	0.20	5.30	0.18	5.58	0.19	6.80	0.18	7.57	0.19
2	C	4.40	0.15	5.01	0.13	5.25	0.14	5.50	0.13	6.70	0.11	7.43	0.10
3	A	4.57	0.14	5.22	0.13	5.45	0.13	5.76	0.12	7.11	0.11	7.85	0.11
CPA (peak area/migration time)													
1	A	1.91	2.54	1.36	1.30	1.86	2.49	1.36	0.91	1.43	1.16	1.24	2.71
1	B	1.88	1.54	1.36	1.84	1.77	1.03	1.35	1.61	1.43	2.11	1.25	1.00
2	A	1.94	2.32	1.31	2.52	1.83	2.57	1.33	1.52	1.50	1.19	1.24	2.64
2	B	1.91	2.85	1.38	2.89	1.81	2.70	1.31	1.30	1.52	2.92	1.24	2.00
2	C	1.92	2.42	1.31	3.01	1.79	1.90	1.33	1.21	1.48	1.76	1.25	2.86
3	A	2.59	1.91	1.78	1.48	2.56	3.03	1.85	1.48	2.07	0.89	1.91	2.19

[a] Conditions: BGE: 4 m*M* NDC–14.4 m*M* Bis-Tris–0.2 m*M* TTAB, pH 6.2; injection: pressure for 10 s; run mode: constant current at 6.6±0.2 μA for 7 min, then constant voltage at −15 kV. Other conditions as specified in the Experimental section. Note that capillary No. 3 was installed in the cartridge with an aperture of 100 μm×800 μm.

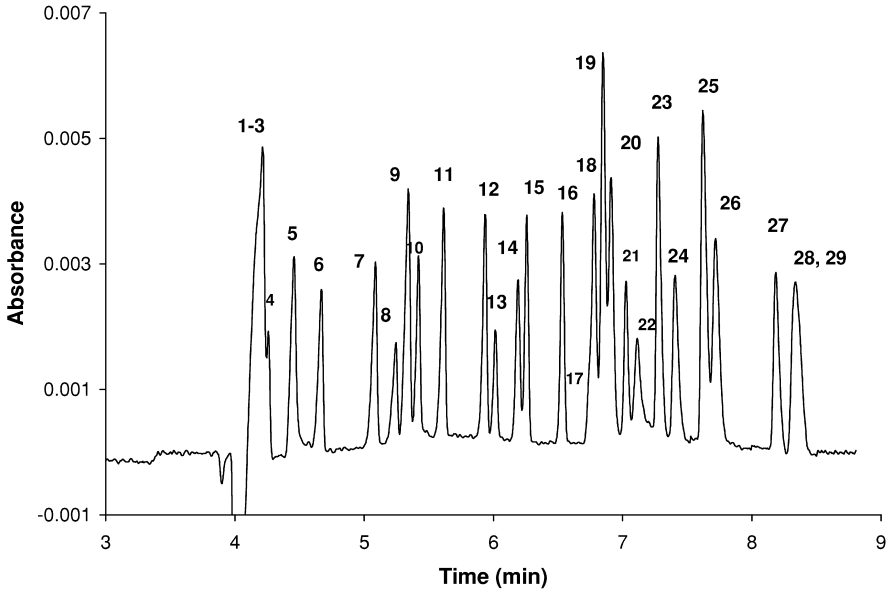

Fig. 2. CE separation of inorganic and organic acids under the optimized conditions. Peaks (each 2 mg/l unless given otherwise): 1=bromide; 2=chloride (1 mg/l); 3=sulfate; 4=nitrate; 5=oxalate; 6=chlorate; 7=malonate; 8=fumarate; 9=formate; 10=malate; 11=succinate; 12=glutarate; 13=phthalate; 14=methanesulfonate; 15=adipate; 16=pimellate; 17=pyruvate; 18=suberate; 19=glycolate; 20=acetate; 21=azeliate; 22=glyoxylate; 23=sebacate; 24=phosphate (3 mg/l); 25=lactate; 26=propionate; 27=hydroxyisobutyrate; 28=butyrate and 29=benzoate. Other experimental conditions as in Fig. 1.

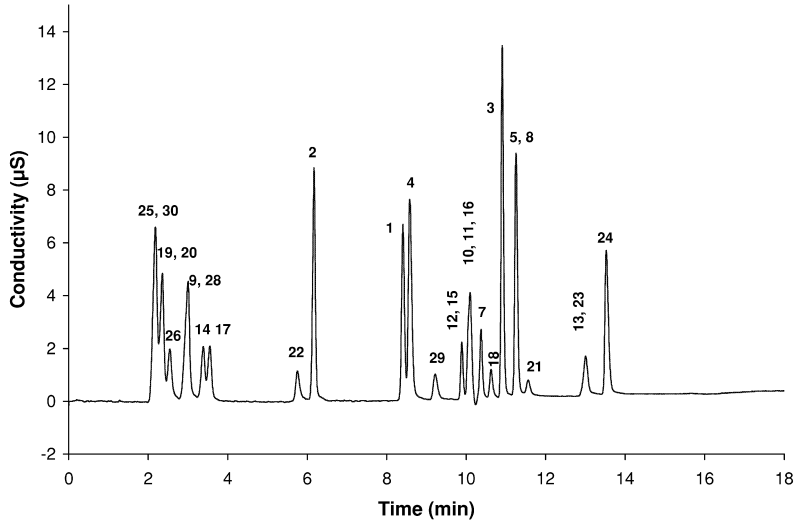

Fig. 3. Ion chromatographic separation of inorganic and organic anions using an IonPack AS11 column and sodium hydroxide gradient elution (after blank subtraction). Peaks: 30=fluoride (0.5 mg/l), concentration of all organic acid (1.0 mg/l); other peaks and concentration as in Fig. 2. Other conditions as in Experimental section.

and oxalate (peak 5); phthalate (peak 13) and sebacate (peak 23).

3.2.2. Repeatability and reproducibility

To determine the repeatability and reproducibility of migration times and CPAs, a mixture of organic acids at the concentration of 2 mg/l was analyzed nine times on a single day on different days over 6 months using three different capillaries. The short- and long-term precision of the migration times and corrected peak areas for some representative peaks are presented in Table 1. As expected, migration time variations were usually smaller intra-day (RSD<0.2%) than those between days. The day-to-day reproducibility of migration times using different capillaries (RSD<3%) was affected by changes of the capillary surface conditions. The variability in BGE preparation could contribute to this inconsistency as well.

Injection precision in CE is generally poorer than that for IC due to nl volumes of sample injected into the capillary. Nonetheless, good intra-day precision of the CPA (1–3%) was obtained when a 10-s injection of the sample with a 2-s co-injection of BGE plug was applied, as can be seen in Table 1. Good reproducibility of CPA from batch-to-batch of BGE and capillary-to-capillary was also obtained. The sensitivity was higher by about 40%, when capillary No. 3 was installed in a cartridge with a larger aperture of 100 μm×800 μm; thus in further experiments, these capillary cartridges were used. The overall results indicate that the CE method had a high degree of precision and could be used adequately for the quantitative measurement of low-M_r carboxylic acids in the samples of interest.

3.2.3. Detection limits, sensitivity and linearity

The detection limits for the acids tested ranged from 50 to 180 μg/l (Table 2) using a 10-s pressure injection. Poorer detection limits were obtained for analytes like pyruvate, phthalate or benzoate due to their absorptivity at 214 nm. The proposed CE method provides equivalent or better detectability than those reported previously using other probes for indirect UV detection [44]. However, the CE detection limits using pressure injection are typically an order of magnitude higher than those achieved by IC with suppressed conductivity detection.

If additional sensitivity was desirable for better detection limits, one could either employ a bigger injection volume or use electrokinetic injection. As expected, the sensitivity increased with longer injection time but the resolution between some peaks decreased as the injection time was increased from 10 s to 60 s. Based on the observed results, up to 30 s of hydrodynamic injection could be used without any major deterioriation in the resolution. The detection limits obtained by electrokinetic injection at 10 kV for 10 s were almost one to two orders lower than those obtained by applying hydrodynamic injection for 10 s (Table 2). In hydrodynamic injection, sample volume loaded is nearly independent of the sample matrix but depends on the capillary dimensions, BGE and sample viscosity, applied

Table 2
Comparison of the detection limits[a]

Analyte	Detection limit (μg/l)			Analyte	Detection limit (μg/l)		
	CE (pressure, 10 s)	CE[b] (10 kV, 10 s)	IC (25 μl)		CE (pressure, 10 s)	CE[b] (10 kV, 10 s)	IC (25 μl)
Oxalate	75	ND[c]	3	Glycolate	68	6	ND
Malonate	69	4	ND	Pyruvate	160	10	14
Formate	52	6	8	Suberate	95	4	12
Malate	90	6	ND	Acetate	47	4	9
Succinate	54	3	14	Glyoxylate	137		17
Phthalate	110	9	14	Lactate	85	5	ND
Methanesulfonate (MSA)	81	4	18	Propionate	70	4	22
Glutarate	72	3	9	Benzoate	180	10	ND

[a] Calculated at the 95% confidence level (DL=$t_{n-1}s$, where s is standard deviation).
[b] Determined in the presence of 10 mg/l sulfate.
[c] ND, Not determined.

pressure and time. However, in electrokinetic injection, the amount loaded is dependent on the EOF, conductivity and viscosity of BGE and sample, applied time and voltage level, and electrophoretic mobilities of analytes. Thus, injection bias exists with the more mobile species being loaded to a greater extent, and the sensitivity generally suffers with increasing concentration of matrix ions. For example, it was found that the presence of 20 mg/l of sulfate in a sample containing analytes at a concentration of 250 μg/l resulted in approximately 90% decrease in CPA in comparison to samples without sulfate. Because of the strong dependence of electrokinetic injection efficiency on specific nature of the sample matrix, quantification requires the use of an internal standard [45].

CPA normalized with the internal standard (I.S.) could compensate for bias in electrokinetic injection. In our study pentasulfonic acid was used as an I.S., and a peak area ratio variance across the six mixtures (containing sulfate ranging from 1 to 25 mg/l) of less than 20% was achieved. This degree of accuracy is sufficient for most environmental screening applications at the trace levels. However, for the best quantitative analysis, the pressure injection mode is recommended.

Linearity was determined by analyzing standards at different concentrations in the range 0.5–10 μg/ml using 10-s pressure injection and in the range 0.1–1.0 μg/ml using 30-s pressure injection, and in the range 0.04–0.4 μg/ml using electrokinetic injection (10 kV, 10 s) with two injections for each concentration level. The correlation coefficients for linear best fit were better than 0.998. Linearity at higher concentrations was not investigated.

3.2.4. Accuracy

Preliminary valuation of accuracy was assessed by comparing the results obtained by CE and IC methods. The regression equation for formate analyzed in 91 vehicle emission samples was CE=0.952IC+ 0.006 with correlation coefficient of 0.994 showing an acceptable comparability of the two methods. In addition to regression procedure, a quantitative deviation between these methods for formate was calculated in terms of the relative percentage difference (RPD) between results as follows:

$$\text{RPD}\ (\%) = 100 \cdot (X_{\text{CE}} - X_{\text{IC}})/0.5 \cdot (X_{\text{CE}} + X_{\text{IC}})$$

where X_{CE} and X_{IC} are the measurements of formate concentrations of the same filter extracts using CE and IC, respectively. In general, the RPD was found to be less than ±25% (Fig. 4). However, some definite outlier results were present too. The study to find the source of these differences is under investigation. In addition, the study is in progress to validate the usefulness of the electrokinetic injection mode using internal standard for routine analysis, and the accuracy of the analysis will be established by comparison with the IC method.

4. Applications

Several atmospheric aerosol and vehicle emission samples were analyzed with the CE method developed in this work and compared with those obtained by IC. Figs. 5a and 6a show typical electropherograms of fine airborne particulate matter and diesel emission extracts, respectively. Well-defined electropherograms were obtained without interferences from matrix constituents such as sulfate, nitrate and chloride. However, the determination of oxalate (peak 5) in the presence of inorganic ions (peaks 2–4) at concentrations higher than 40 mg/l would be problematic due to the poor resolution between peaks. A similar problem was observed in the IC analysis (Figs. 5c and 6b). Since the selectivity of CE and IC differed, the complementation of these two techniques strengthened the identification of analyte peaks.

Low-M_r organic acids such as oxalic, malonic, formic, malic, succinic, acetic and lactic acids were identified in rurally collected fine particulate matter by matching their migration times with those of a standard solution. Some unidentified peaks were also detected by both the CE and IC methods. The concentrations of organic acids were about two orders of magnitude lower than those observed for inorganic anions. Oxalic acid was found in all samples with concentrations about 2–5 times higher than those of other carboxylic acids. Malonic and succinic acids were detected in almost every sample. In general, the concentrations of low-M_r carboxylic acids in such samples are in the middle to lower

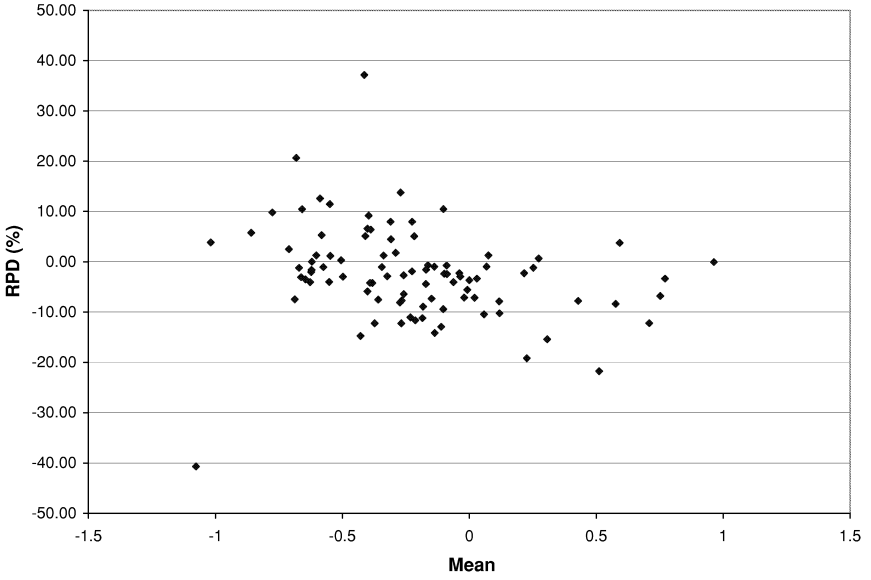

Fig. 4. Visual evaluation for the comparison of the results obtained by CE and IC methods. RPD, Relative percentage difference between results. In order to observe the spread at low concentrations (around zero), the values of the mean concentrations have been transferred to a logarithmic scale.

μg/l range. They are frequently close to or below the detection limits of both CE and IC methods. Therefore, the online concentration of these compounds by electrokinetic injection or sample stacking is desirable. As can be seen in Fig. 5b, several additional species could be detected in such samples when electrokinetic injection was applied. This illustrates the very high sensitivity of this injection mode and capability of detecting trace anions at low μg/l levels often beyond the detection limit of the IC system.

Oxalate, formate, acetate, glycolate, and lactate were identified in diesel emission collected on KOH-coated filters (Fig. 6a). The concentrations of organic acids in extracts, especially formic and acetic acids, were at the mg/l level. Some unidentified peaks were also present. Attempts to identify all unknown peaks in atmospheric aerosol and vehicle emission samples are in progress.

The relative abundance of organic acids in the studied samples is in general agreement with previous results published by other groups [1–6,8–11,14,20,28,29]. Formic and acetic acids were the most abundant monocarboxylic acids. Pyruvic, glycolic and lactic acids were also detected. Studies on molecular distribution of dicarboxylic acids generally showed the predominance of oxalic (C_2) followed by malonic (C_3), and succinic acid (C_4). These acids comprised up to 80% of total dicarboxylic acids in the atmosphere. Dicarboxylic acids with more carbons were reported to be less abundant. It has been also reported that monoacids are mostly present in the vapor phase, whereas diacids are mostly associated with particulates. However, some low-M_r dicarboxylic acids (i.e., oxalic) have sufficient vapor pressure under elevated temperature conditions to also exist in the vapor phase as evidenced in the analysis of diesel emission captured on KOH-coated filters.

5. Comparison of CE and IC methods

Some general advantages of CE over IC discussed elsewhere [14,46] and applicable here include better separation efficiency, lower consumption of chemical reagents, less waste, lower cost of operation, and shorter analysis time. Although there is generally the advantage of better precision for IC in comparison with CE, this has no impact on the precision

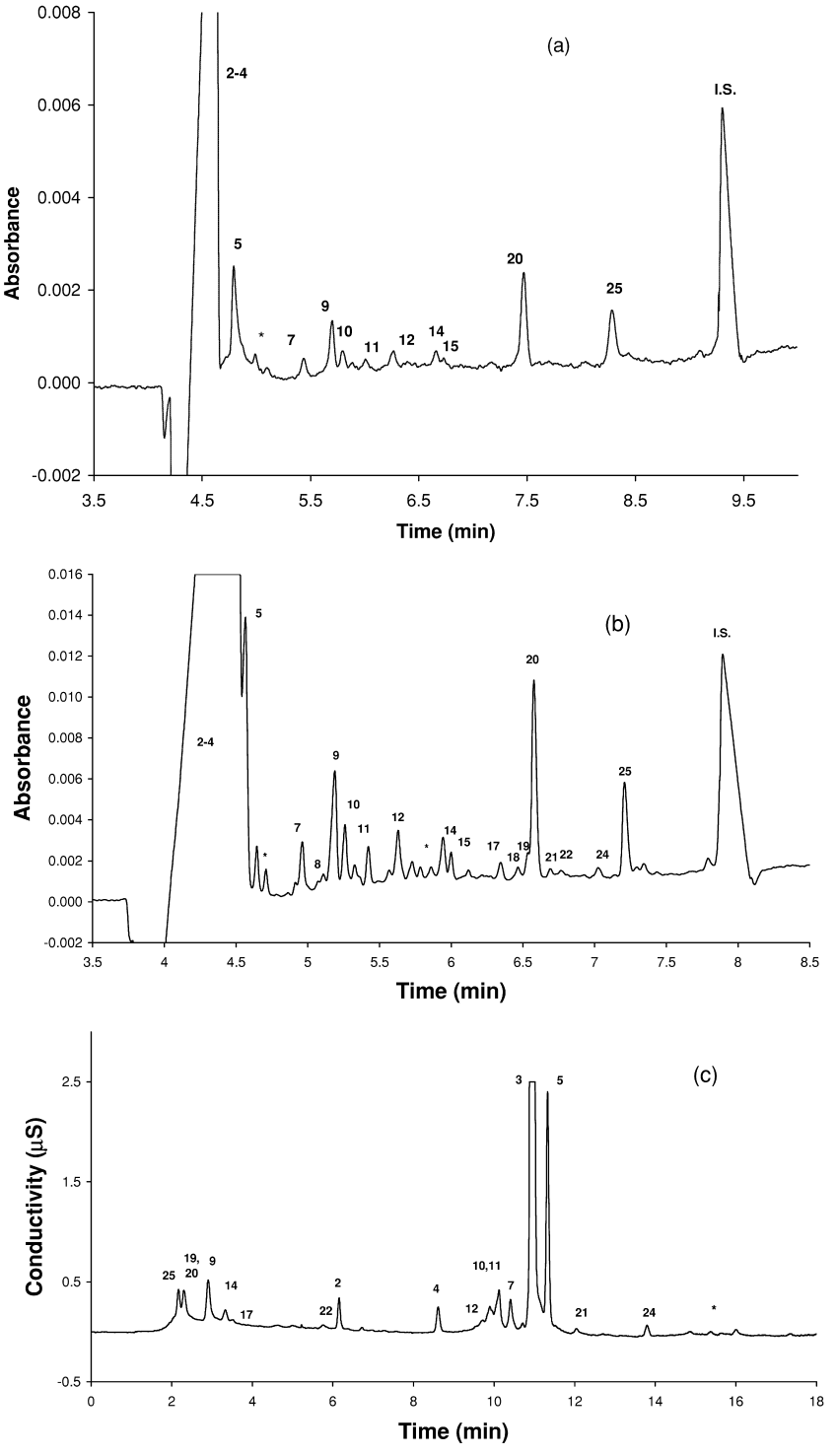

Fig. 5. Typical electropherograms using pressure injection for 30 s (a), electrokinetic injection at 10 kV for 10 s (b), and ion chromatogram of fine airborne particulate matter extract (c). Peaks and conditions as in Figs. 2 and 3, *=unidentified peaks, I.S.=internal standard (pentasulfonate).

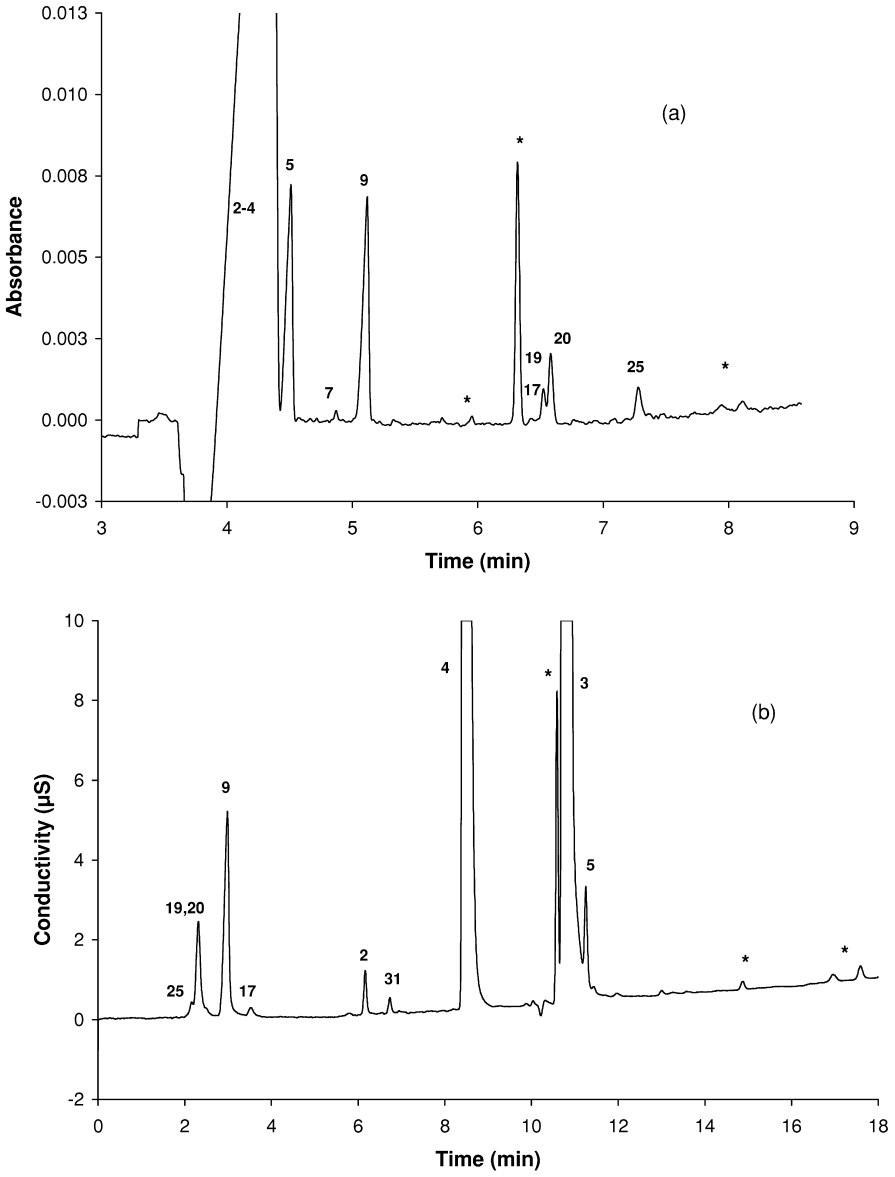

Fig. 6. Typical electropherogram using pressure injection for 10 s (a), and ion chromatogram of diesel emission extract (b). Peaks and conditions as in Figs. 2 and 3; 31 = nitrite, * = unidentified peaks.

achieved in this developed method. Also, the linearity and long-term reliability are similar. In terms of detection limits, IC has an advantage over CE. The use of electrokinetic injection enhances CE sensitivity but it matrix dependent. Nevertheless, CE with its high efficiency and different selectivity mechanism has a wider separation range and allows the analysis of a larger variety of low-M_r carboxylic acids of interest. The two methods are complementary and thus able to cross-validate each other.

6. Conclusions

In this work, a reliable CE method with indirect UV detection using a buffered BGE for the de-

termination of a large number of low-M_r carboxylic acids has been developed. The method (with the BGE containing 4 m*M* NDC as an UV-absorbing anion, 0.2 m*M* TTAB as an EOF modifier and 14.4 m*M* Bis-Tris to adjust pH at 6.2) is easy, selective (for organic acids), rapid and inexpensive. Reliability of the analysis for low-M_r organic acids is improved by using the buffered BGE, proper rinse steps, and constant current mode. Separations are robust with migration time variations less than 3% RSD on a day-to-day basis, using different capillaries and performed by different analysts. Detection limits are at the tens of μg/l level using a pressure injection. Better sensitivity is possible when electrokinetic injection is used. Research on applying electrokinetic injection for the accurate analysis of low-M_r organic acids is in progress.

The analytical validation shows that the CE method can be advantageously applied to monitoring a variety of mono- and dicarboxylic acids in atmospheric aerosol and vehicle emission samples. In contrast, the conventional IC separation of these anions shows fewer resolved peaks in a longer analysis time. Nevertheless, the application of two different techniques will usually be needed to confirm the identification of analytes present in complex samples. No sample treatment is needed for the analysis of atmospheric aerosol samples collected on PTFE filters. However, the high ionic strength of vehicle emission samples collected on KOH-coated filters requires the elimination of high hydroxide concentration before both CE and IC analysis. Future work will be directed to further improve detection limits and identify unknown peaks.

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