Determination of Aromatic Acids and Nitrophenols in Atmospheric Aerosols by Capillary Electrophoresis

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Abstract

A capillary zone electrophoresis method is developed for the determination of aromatic organic acids and nitrophenols in atmospheric aerosols. The procedure is based on sampling atmospheric particulate matter on quartz fiber filters and the extraction and analysis of the extracts by capillary electrophoresis. Separation conditions are optimized by varying the pH and acetonitrile content of the electrolyte buffer. Separations in a 20% acetonitrile–20mM borate mixture (pH 9.9) are able to resolve all of the geometric isomers of hydroxybenzoic acid, phthalic acid, benzenetricarboxylic acid, and nitrophenol as well as 1,2,4,5-benzenetricarboxylic acid, *m*-toluic acid, and sulfosalicylic acid. A buffer consisting of 11% acetonitrile–20mM borate (pH 9.9) is found to be most suitable for the analysis of atmospheric aerosol samples. Detection limits are in the order of 40 to 130 ng/mL. Intersample migration time reproducibility is generally better than 1.5%, with day-to-day variations under 3%. A general extraction scheme using diethyl ether–HCl in combination with a preconcentration step is developed. Recoveries of spiked standards range from 59% to 102%, with relative standard deviations ranging from 2% to 17% for five determinations. The method is applied towards the analysis of ambient aerosol samples as well as vehicle emission studies with promising results, thus showing it to be a potential complement to already existing methodology for the analysis of organic acids and nitrophenols in atmospheric aerosols.

Introduction

Atmospheric particulate matter (APM) is comprised of a highly complex chemical mixture containing organic and inorganic compounds derived from both anthropogenic and biogenic sources. The photochemical oxidation of directly emitted volatile organic compounds (VOC) results in the formation of both oxygenated and nitrated species, of which some of the partition into the aerosol phase (provided their vapor pressure is low enough) results in the formation of secondary organic aerosol (SOA) (1–4). Numerous aliphatic, hydroxy, keto, diterpenoid, polycarboxylic, and aromatic-containing organic acids (ACOAs) have been reported as components of SOA (5–9). Interest in the determination of these species stems from a number of issues related to atmospheric chemistry and air quality including acid precipitation, adverse health effects of particulate matter, air-quality monitoring, and understanding the origin as well as the fate of the corresponding VOC precursors.

Typically, the measurement of low-molecular-weight (MW) carboxylic acids in the atmosphere has involved ion chromatography (IC) with suppressed conductivity or UV detection. Trace levels of carboxylic acids in atmospheric samples have also been determined by gas chromatography (GC) following the formation of suitable derivatives such as methyl or ethyl esters. A comprehensive up-to-date review of all methods used for the determination of low-MW carboxylic acids in ambient air and vehicle emissions was recently published by Dabek-Zlotorzynska et al. (10). Overall, GC remains the method of choice for the analysis of complex environmental mixtures because of its high peak capacity, sensitivity, and its ease of coupling with mass spectrometry (MS) for reliable peak identification.

Recently, capillary electrophoresis (CE) has received considerable attention in this field as a potential complement to IC and GC–MS methods. Krivácsy et al. (11) used chromate as a background electrolyte to measure inorganic ions and several low-MW organic acids in atmospheric aerosols by CE with indirect photometric detection. Dabek-Zlotorzynska et al. (12,13) used 1,6-naphthalene-dicarboxylic acid and pyromellitic acid for the determination of organic acids and inorganic ions respectively in APM and vehicle emission samples. Kibler and Bächmann (14) achieved low nanomolar detection limits of several aliphatic carboxylic acids by derivatization with 4-aminofluorescein followed by CE–laser-induced fluorescence analysis. ACOAs have received considerably less attention (15). In order to solve the problem of separating many geometric isomers with very similar ionic mobilities in the context of answering inter alia more general questions concerning selectivity in CE separations, the influence of organic solvents (16,17), imidazole-coated capillary columns with metal and cyclodextrin buffer additives (18), micellar electrokinetic capillary (15), and ionic strength (19) has been studied by various workers.

In this work, the effects of organic solvents and pH were inves-

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tigated on the separation of various polycarboxylic and hydroxy aromatic acids as well as nitrophenols, including all positional isomers of the foregoing classes of compounds. We present a scheme for the extraction of ACOAs from atmospheric aerosols collected on quartz fiber filters, followed by counterelectroosmotic capillary zone electrophoresis (CZE) separation with diode-array detection (DAD).

Experimental

Apparatus

All CE experiments were performed on a Hewlett-Packard (Waldbronn, Germany) 3D-CE instrument equipped with a photo-DAD and buffer replenishment system using HPCE software (Version 6.1) for data acquisition and processing. Chromatographic Specialties (Brockville, Ontario, Canada) fused-silica capillaries with an inner diameter of 50 µm, an outer diameter of 365 µm, and a total length of 48.5 cm (40 cm to the detector) were used in addition to bubble-cell capillaries (Agilent Technologies, Mississauga, Ontario, Canada) with an inner diameter of 75 µm (200-µm light path in detection cell), an outer diameter of 365 µm, and a total length of 48.5 cm (40 cm to the detector). All separations were carried out in the counter-electroosmotic mode at +30 kV with the capillary temperature controlled at 25.0°C ± 0.02°C using the air-cooling system of the instrument. The signal was at 199 nm, and the injections were 200 mbar/s.

Reagents and standards

All chemicals used in this work were of analytical-reagent grade from Sigma-Aldrich (Oakville, Ontario, Canada) and used without further purification. Purified water (18 MΩ) from a Milli-Q water purification system (Millipore Canada, Mississaugua, Canada) was used to prepare all solutions. Stock solutions of carboxylic acids, sulfosalicylic acid, and phenols (400–1000 µg/mL) were prepared by dissolving an appropriate amount of the compound or its sodium salt in deionized water. All solutions were stored at 4°C. All solvents and solutions for CE analysis were filtered through 0.45-µm poly(tetrafluoroethylene) (PTFE) filters (Chromatographic Specialties).

Preparation of capillary columns

New capillaries were rinsed with methanol (10 min), deionized water (5 min), 1M HCl (10 min), deionized water (5 min), 1M NaOH (30 min), and deionized water (5 min). On a daily basis, capillaries were conditioned by flushing with 0.2M HCl (2 min), 1M NaOH (10 min), 0.2M NaOH (5 min), deionized water (1 min), and finally with running buffer (5 min) followed by an application of 30 kV (15 min). At the end of each day, capillaries were rinsed with 0.1M NaOH (3 min) and deionized water (5 min) and then followed by flushing with air (3 min). In between runs, capillaries were flushed with 0.2M NaOH (1 min), deionized water (1 min), and a buffer solution (2 min). Buffer replenishment was carried out after every run. Sample injection was performed hydrodynamically by applying a pressure of 25 mbar for 8 s in the case of separations using 75-µm-i.d. bubble capillaries and 25 mbar for 18 s in the case of 50-µm-i.d. regular capillaries. Both of these injection modes deliver an injection plug of 8.1 mm in length, thus corresponding with volumes of 36 and 20 nL for the capillaries, respectively. Injection volumes and plug lengths were calculated using Beckman (Fullerton, CA) CE Expert software Version 1.0.

After several key method development experiments were performed, it was learned that the flushing of capillaries with 0.2M HCl in the morning prior to NaOH conditioning decreased migration times considerably and also improved reproducibility.

Sampling and sample preparation

Aerosol particles (diameter < 10 µm) were collected on 8- × 10-inch Quartz fiber filters (Pallflex Products Corp., Putnam, CT) using a Hi-Vol air sampler equipped with a PM10 head. The average flow rate was 1.13 m^3/min, and generally samples were collected for 24 h. Following sampling, filters were weighed, divided into eight parts, and stored at –20°C in glass jars filled with nitrogen gas. One-eighth of the total filter was used for each extraction. Prior to sampling, new filters were baked at 750°C in a large chamber muffle furnace (Fisher Scientific Model 550-58, Napean, Ontario, Canada) to remove organic contaminants.

Buffer preparation

All buffers were prepared from 100mM boric acid stock solutions by dilution with water and the appropriate amount of organic solvent. The pH was adjusted with 0.5M NaOH. The resulting mixture was filtered through a 0.45-µm PTFE filter (Chromatographic Specialties).

Extractions

The extraction method used was a modified version of that devised by Fung and Grosjean (20). Briefly, after the addition of 250 ng *m*-toluic acid as the internal standard (IS) and 1 mL 0.1M HCl to acidify the solution, samples were extracted with 10 mL high-performance liquid chromatography-grade diethyl ether by means of mechanical stirring for 1.5 h. The extraction time was found to be necessary in order to completely pulverize quartz fiber filters and render them amenable to separation from the aqueous layer by centrifugation. Pulverized quartz and ether mixtures were then transferred to a capped glass tube for centrifugation. Following the separation of the phases, the ether layer was transferred to a fresh test tube. A 2-mL volume of diethyl ether was added to the residual aqueous HCl–quartz fiber layer. The solution was vortexed and again separated by centrifugation. The ether layers were then combined and this step was repeated once more. The combined ether layers were evaporated to dryness under a stream of pure nitrogen gas, and redissolved in 100 µL 2mM boric acid (which was adjusted to pH 9.9 with sodium hydroxide) containing 1 µg sulfosalicylic acid as a second IS. Because the procedure described in this study also extracts neutral substances ubiquitous to aerosols (many of which do not dissolve in aqueous borate following nitrogen blowdown), it was necessary to remove these prior to CE analysis in order to prevent capillary blockage. A 45-µm-pore-diameter PTFE filter was cut to an outer diameter of 4 mm and placed inside a 500-µL gastight syringe at the needle end. Samples were then loaded using long-tipped Pasteur pipettes through the plunger end of the

syringe and filtered into microinsert glass vials for CE analysis.

Results and Discussion

Effect of pH

Typically, simple organic anions such as the ACOAs used in this study have mobilities opposite to the electroosmotic flow (EOF) direction in uncoated fused-silica capillaries. With a positive voltage applied, the EOF moves towards the cathode where the detection window is located. Because the EOF is very fast along side the alkaline pH values, anions eventually end up being dragged across the detection window through the movement of the EOF. We refer to separations of this type as counter-electroosmotic. Alternatively, a cationic surfactant can be added to the electrolyte in order to reverse the EOF; application of a negative voltage then results in the migration of anions towards the detector. In early experiments, we found the latter approach to provide an unsatisfactory resolution of the ACOAs and phenols of interest in this study. The counter-electroosmotic approach was used for all experiments reported.

The effect of pH on the resolution of the 17 compounds used in this study was investigated in a 20mM borate buffer. Figure 1 shows a plot of electrophoretic mobility as a function of pH obtained from these experiments. Worth noting is the comigration of phthalate and isophthalate and the poor separation of

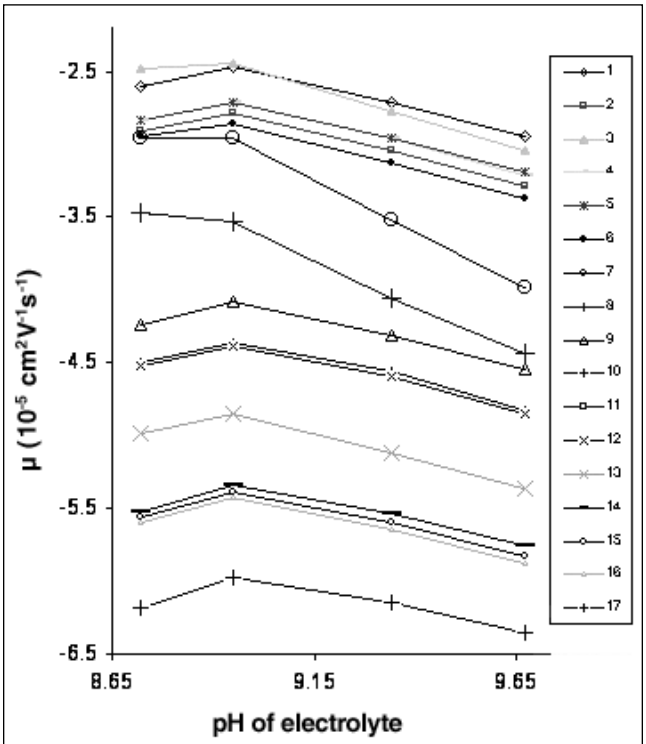

Figure 1. Electrophoretic mobility as a function of pH for 14 acids and three nitrophenols tested in a 20mM aqueous borate buffer: *m*-toluate (IS1), 1; *o*-nitrophenol, 2; *m*-nitrophenol, 3; *p*-nitrophenol, 4; benzoate, 5; 2-hydroxybenzoate, 6; 3-hydroxybenzoate, 7; 4-hydroxybenzoate, 8; 4-methylphthalate, 9; *p*-phthalate, 10; *m*-phthalate, 11; *o*-phthalate, 12; sulfosalicylate (IS2), 13; 1,2,3-benzenetricarboxylate, 14; 1,2,4-benzenetricarboxylate, 15; 1,3,5-benzenetricarboxylate, 16; and 1,2,4,5-benzenetetracarboxylate, 17.

p-nitrophenol from benzoate. The three benzenetricarboxylate isomers (4-methylphthalate, sulfosalicylate, and 1,2,4,5-benzenetetracarboxylate) were well-separated at all pH values tested. The three hydroxybenzoate isomers were separated at pH values exceeding 8.85. 3-Hydroxybenzoate and 4-hydroxybenzoate showed significantly increased mobilities relative to the other compounds as the pH of the buffer approach values conducive to the dissociation of the hydroxyl group (pK_{a_2} = 9.61 for 3-hydroxybenzoate, 9.31 for 4-hydroxybenzoate, and 13.74 for 2-hydroxybenzoate). This allowed for a complete resolution of 3-hydroxybenzoate from 2-hydroxybenzoate at these pH values. Among the nitrophenols studied, 3-nitrophenol (pK_a = 8.40) experienced the greatest increase in mobility with increasing pH. Its dissociation constant was higher compared with the other isomers (7.15 for *p*-nitrophenol and 7.23 for *o*-nitrophenol); therefore, the hydroxyl group of 3-nitrophenol underwent full deprotonation at higher pH values than the other isomers. All pK_a values cited were obtained from reference 21.

Effect of organic solvent and pH

Several studies (16,17,22,23) report the use of organic solvents to improve separations under counter-electroosmotic CZE conditions (16,17,22,23). In early experiments, methanol was observed to have a very similar effect on resolution as acetonitrile but gave considerably longer analysis times and was not tested further. Separation of the 14 acids and three nitrophenols investigated in this work was then tested in a buffer consisting of 11% acetonitrile–20mM borate as a function of increasing pH. We observed a complete resolution of the three phthalate isomers and 4-methylphthalate as well as sulfosalicylate and 1,2,4,5-benzenetetracarboxylate at all values of pH tested in the range of 9 to 10.3. The three hydroxybenzoate isomers were well-separated at pH 9.3 and higher. In general, the 17 compounds tested showed the same pattern of changes in electrophoretic mobility as a function of pH similar to that shown in Figure 1, with the 1,2,4-benzenetricarboxylate and 1,3,5-benzenetricarboxylate isomers being notable exceptions, which comigrated at pH values below 9.3 and showed partial resolution of 0.35 at pH 9.6, 0.53 at pH 9.9, and 0.55 at pH 10.3. *M*-Nitrophenol comigrated with *m*-toluate at pH 9.3 (which is analogous to the situation at pH 9.05 in Figure 1); otherwise, the three nitrophenol isomers were also well-separated. It should also be noted that the combination of a very alkaline buffer (pH > 10) and a 75-µm-i.d. capillary is only tolerable with an organic additive in the buffer, capillary overheating and aberrant baselines result otherwise.

Separations were subsequently tested in 20mM borate (pH 9.9) with increasing concentrations of acetonitrile as the organic solvent additive. As shown in Figure 2, a greater percentage of acetonitrile led to a slightly decreased EOF and increased migration times for most compounds. In regards to resolution, the separation of most compounds appeared largely unaffected by the increased percentage of acetonitrile with the exception of the benzenetricarboxylate isomers, which showed an almost linear improvement in resolution with an increasing acetonitrile content of the buffer (Figure 2). All compounds tested were fully resolved in a 20% acetonitrile–20mM borate (pH 9.9) buffer. Ostensibly, this is the optimum buffer for the analysis of the compounds investigated, providing that no interfering sub-

stances are present. Further increasing the percentage of acetonitrile results in significant peak broadening and decreased sensitivity. As expected, early eluting slow-moving peaks were separated more efficiently without noticeable peak broadening. Theoretical plates for separation in 11% acetonitrile–20mM borate (pH 9.9) ranged from 205561 for 3-hydroxybenzoate to 76016 for 1,2,4,5-benzenetetracarboxylate. Separations in 20% acetonitrile–20m*M* borate (pH 9.9) were correspondingly less efficient because of longer migration times and slightly broader peaks.

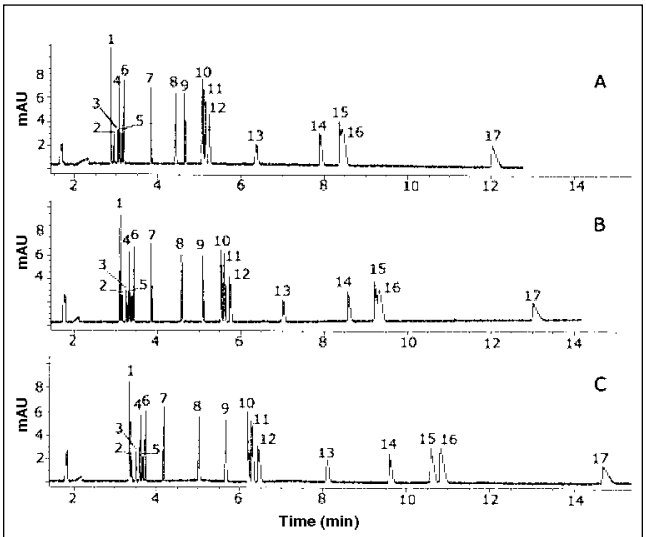

Figure 2. Separation of 14 acids and 3 nitrophenols in 20mM borate (pH 9.9) with (A) 11% acetonitrile, (B) 16% acetonitrile, and (C) 20% acetonitrile: *m*-toluate (IS1), 1; *m*-nitrophenol, 2; *p*-nitrophenol, 3; benzoate, 4; *o*-nitrophenol, 5; 2-hydroxybenzoate, 6; 3-hydroxybenzoate, 7; 4-hydroxybenzoate, 8; 4-methylphthalate, 9; *p*-phthalate, 10; *m*-phthalate, 11; *o*-phthalate, 12; sulfosalicylate (IS2), 13; 1,2,3-benzenetricarboxylate, 14; 1,2,4-benzenetricarboxylate, 15; 1,3,5-benzenetricarboxylate, 16; and 1,2,4,5-benzenetetracarboxylate, 17.

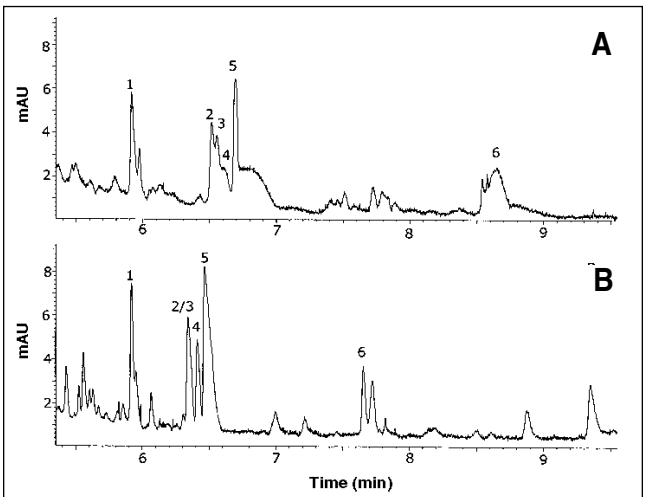

Figure 3. Electropherogram of an extract of APM analyzed using (A) 20% acetonitrile–20mM borate (pH 9.9) and (B) 11% acetonitrile–20mM borate (pH 9.9). Only the region in the vicinity of the phthalate peaks is shown for clarity. Peak migration times are aligned with respect to 4-methylphthalate. Peaks: 4-methylphthalate, 1; *p*-phthalate, 2; unidentified, 3; *m*-phthalate, 4; *o*-phthalate, 5; and sulfosalicylate, 6.

Effect of buffer composition on the analysis of environmental aerosol samples

Although the standard mixtures we used to develop an optimized separation contained all the compounds we targeted for analysis, ambient samples can include a significant number of components that may interfere with the separation and quantitation of the analytes. For this reason, several ambient samples were analyzed using different buffers. Indeed, the 20% acetonitrile–20mM borate (pH 9.9) buffer was observed to be less suitable for the analysis of real samples than one would expect from the results we obtained for artificial mixtures. Meta- and orthophthalate peaks often eluted grossly distorted, even though the purity of their UV spectra gave no indication of comigrating compounds. A possible reason might be overlap with other acids present at high concentrations (acids that are not detectable by UV–vis absorption). The sulfosalicylate peak was also observed to be problematic. Figure 3 shows partial electropherograms of aerosol samples obtained with both the 20% acetonitrile and 11% acetonitrile 20mM borate (pH 9.9) buffers. Clearly, the separation using the 11% acetonitrile buffer was superior to the results obtained with the 20% acetonitrile buffer, even though the *p*-phthalate peak was found to overlap with an unidentified compound. Through the analysis of UV spectra obtained from different parts of this peak (i.e., the unknown was in the shoulder, *p*-phthalate was in the tail, and the rest of the peak contained a mixture of both), we observed that the interference had no significant absorbance at 240 nm (the second absorbance maximum being *p*-phthalate). This wavelength was then chosen as the optimal wavelength for the analysis of this compound. A similar analysis for 2-hydroxybenzoate (which we found in most of our ambient samples) showed a fronting peak, thus pointing to the presence of another unresolved and unidentified substance. A spectral analysis of this peak showed better selectivity at 305 nm (the third absorbance maximum being 2-hydroxybenzoate); however, the sensitivity proved unsatisfactory. A reasonable compromise between selectivity and sensitivity was obtained by using peak height instead of peak area at 201 nm.

The 1,3,5-benzenetricarboxylate isomer was observed to be absent from most (> 99%) of the ambient samples analyzed. Thus, the improved resolution of the 20% acetonitrile–20mM borate buffer (pH 9.9) was not requisite for ambient measurements. The 11% acetonitrile buffer did however allow sufficient resolution between the three benzene–tricarboxylate isomers in order to allow for their identification (Figure 2A), should all three be encountered simultaneously. Furthermore, yet another unidentified component of aerosol extracts (a compound well-resolved with the 11% acetonitrile buffer) comigrated with *m*-toluate (our IS) when the 20% acetonitrile buffer was applied. Thus, for the analysis of ambient APM samples, a 20mM pH 9.9 borate buffer containing 11% acetonitrile was most suitable for the analysis of the target analytes.

Detection limits, reproducibility, repeatability, and linearity

The detection limits (defined in this study as a signal-to-noise ratio of three) were determined by peak height, and ranged from 40 to 130 ng/mL (Table I) using an 8-s, 25-mbar injection. This corresponded with a plug length of 8.1 mm (2.0% of the capillary length to the window) and delivered a volume of 36 and 20 nL

with the 75- and 50-µm capillaries, respectively. Bigger injection volumes were typically observed to give poorer resolution, especially in light of the aforementioned only marginally resolved unidentified compounds. The plug length, and thus injection volumes, could be increased without a significant loss of resolution by using longer capillaries; however, this would be at the expense of longer analysis times.

Table I. Detection Limits Obtained with the Proposed CE Method*

Compound	Detection wavelength (nm)	75-µm-i.d. Bubble-cell capillary (ng/mL)	50-µm-i.d. Straight capillary (ng/mL)
2-Nitrophenol	191	68	166
3-Nitrophenol	191	62	133
4-Nitrophenol	405	76	146
m-Toluate	199	41	70
Benzoate	192	41	68
2-Hydroxybenzoate	201	41	91
3-Hydroxybenzoate	201	48	97
4-Hydroxybenzoate	196,**280**	47,**91**	103,**187**
4-Methylphthalate	200	49	111
p-Phthalate	190,**239**	40,**115**	118,**256**
m-Phthalate	206	42	115
o-Phthalate	195	55	176
Sulfosalicylate	208	64	136
1,2,3-Benzenetricarboxylate	200	88	214
1,2,4-Benzenetricarboxylate	201	64	158
1,3,5-Benzenetricarboxylate	204	71	187
1,2,4,5-Benzenetetracarboxylate	207	128	300

* The wavelengths in boldface are those selected for the analysis of ambient samples (see text).

Linearity was determined by analyzing standards at different ratios relative to the *m*-toluic acid IS in the range of 10 to 5000 ng per 1000 ng IS for all compounds except *o*-phthalate, in which the calibration was performed in the range of 100 to 20000 ng in order to be compatible with the levels in ambient samples. The correlation coefficients for the linear least square fits for the calibrated concentration range were always better than 0.998, which was satisfactory.

The reproducibility of migration times and repeatability of peak-area ratios relative to the IS were determined for three CZE analyses of standard solutions. Results that were obtained at six different amounts of standards ranging from 10 to 5000 ng (10,000 for *o*-phthalate) are reported in Table II. The relative standard deviation (RSD) of the migration times was in the order of 0.13% to 0.60%, regardless of the concentration analyzed. The RSDs of the peak-area ratios (relative to the IS) fell in the range of 0.2% to 8%, which was satisfactory for quantitative purposes. There were small (but nevertheless significant) differences in the range of 0.02% to 1.5% (the highest value being that for *o*-phthalic acid) between the migration times of the standards and samples. By aligning the two ISs used in this study, it was possible to minimize this difference to 0.1–0.6%. In view of the complex composition of aerosol samples in general, we believe the spectral information from the DAD to be essential in order to identify analyte peaks beyond reasonable doubt and monitor possible interferences. This is especially true when samples from different sources are to be analyzed and compared.

Strictly speaking, for the quantitation of the analytes with oncolumn detection, the peak areas have to be corrected for changes in the migration time. However, although the RSDs of the migration times for the sample batches containing up to 35 runs within one day were always less than 1.5% for all compounds (except pyromellitic acid, which on one day containing 25 sample runs had an RSD of 2.6%), these differences were small compared with other factors determining the overall uncertainty of the procedure. Moreover, calibration based on ISs to some extent compensates for changes in migration times, because in one electropherogram the relative change in migration time is generally of comparable magnitude for most analytes. Day-to-day reproducibility was better than 2.2% for all compounds (3.0% for

Table II. Overall Validation of the Proposed CE Method in Terms of Precision of Migration Times and Peak-Area Ratios of ACOAs as a Function of the Amount of Standard and the Recoveries of Standards Spiked onto Quartz Fiber Filters Extracted Using the Diethyl Ether–HCl Method Described in the Experimental Section

Amount (ng)	RSD* (T_M† = 5000)	RSD* (T_M‡ = 5000)	%RSD* A/A_{IS} 10	100	500	1000	5000	%Recovery§ Average	RSD**
EOF	0.13	0.04						97.3	5.2
m-Toluic acid (IS1)	0.24	0.00						91.1	1.6
4-Nitrophenol	0.38	0.00	0.65	0.86	1.00	0.37	0.42	101.7	3.9
Benzoic acid	0.25	0.00	1.70	1.60	1.61	1.42	0.86	100.0	5.7
2-Hydroxybenzoic acid	0.26	0.02	1.44	1.64	1.44	1.49	0.50	98.5	4.2
3-Hydroxybenzoic acid	0.29	0.12	3.55	1.45	1.17	0.41	0.47	96.9	5.3
4-Hydroxybenzoic acid	0.32	0.09	6.80	1.62	1.24	1.52	0.81	95.2	13.0
4-Methylphthalic acid	0.33	0.07	5.23	1.12	0.59	0.19	1.07	93.3	14.4
p-Phthalic acid	0.37	0.10	7.53	3.72	1.25	2.20	0.76	98.0	12.3
m-Phthalic acid	0.38	0.09	3.91	3.63	1.14	0.20	0.43	95.0	13.2
o-Phthalic acid	0.38	0.10	2.56	3.37	0.76	0.75	0.14	–	–
Sulfosalicylic acid (IS2)	0.37	0.00	1.74	1.78	2.03	1.32	1.48	59.3	10.2
1,2,3-Benzenetri-carboxylic acid	0.45	0.07	4.18	1.51	1.98	1.60	1.31	99.3	9.8
1,2,4-Benzenetri-carboxylic acid	0.47	0.08	4.88	2.12	0.25	1.15	1.11	91.5	15.2
1,2,4,5-Benzenetetra-carboxylic acid	0.60	0.22	5.38	1.91	0.85	0.53	1.79	61.4	11.7

* Reported RSD values were obtained from triplicate analyses.
† T_M, Migration time.
‡ Migration times with both ISs aligned.
§ A test mixture containing 1 µg of each compound was used for the spike tests.
** Reported RSD values based on five extractions.

1,2,4,5-benzenetetracarboxylate).

Extraction procedure

The extraction method described in this study involved the acidification of quartz fiber filter followed by the extraction of acids and phenols with ether. The most time-consuming part of the method was the mechanical stirring involved in pulverizing the quartz fiber filter to allow for its transfer into a test tube and subsequent centrifugation. Table II shows the extraction recoveries of standards that were spiked onto quartz fiber filters and extracted using this protocol. Extraction efficiencies of the 15 compounds tested ranged from 59% to 101%, with precisions in the range of 1.6% to 17.1% RSD for five extractions. In regards to the compounds with low recoveries (1,2,3-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate), it was likely that the high polarity and low pK_a values of these acids was to blame for their less efficient extractions. The final volumes of the sample extracts were found to vary somewhat (the consequence of handling small volumes). However, the use of ISs allowed for a reliable and easy correction of this problem. In this context, it was important that our IS (*m*-toluate) had an extraction efficiency of 97.3% ± 5.2%.

Typically, the filter segments extracted by our procedure contained particulate matter from approximately 150 m^3 of air. Based on the volume of the concentrated sample, the recoveries (Table II), and the detection limits (Table I), we calculated that the overall detection limit in air was in the range of 0.3 to 1.5 pg/m^3 or 0.2 to 1 pg/g of APM for a 24-h sampling time. These detection limits can potentially be improved by further reducing the final volume of the extract (which we found to be impractical) or extracting larger fractions of the filter (one-eighth of the filter was used for this procedure). However, even without further improvement the detection limits achieved were adequate for most ambient applications, and additional effort would only be required for the analysis of samples from pristine regions (e.g., marine background air).

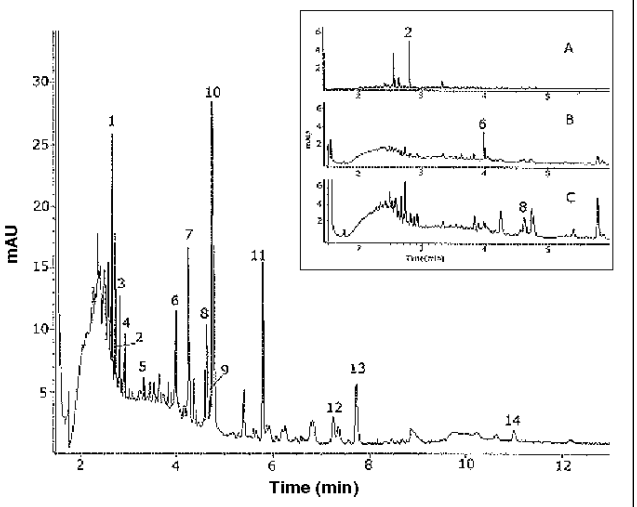

Figure 4. Typical electropherogram of an APM extract obtained under optimized CZE conditions. The inset–signal was at (A) 405 nm, (B) 280 nm, and (C) 239 nm. The peaks were: *m*-toluate (IS1), 1; *p*-nitrophenol, 2; benzoate, 3; 2-hydroxybenzoate, 4; 3-hydroxybenzoate, 5; 4-hydroxybenzoate, 6; 4-methylphthalate, 7; *p*-phthalate, 8; *m*-phthalate, 9; *o*-phthalate, 10; sulfosalicylate (IS2), 11; 1,2,3-benzenetricarboxylate, 12; 1,2,4-benzenetricarboxylate, 13; and 1,2,4,5-benzenetetracarboxylate, 14.

Applications

The method described in this study was applied to the measurement of ACOAs from aerosols collected in Hamilton, Ontario, Canada during the summer of 2001 as well as source tests of vehicle emissions collected inside the Union Station overpass in downtown Toronto, Canada. Figure 4 shows an example electropherogram. In addition to twelve identified compounds, there were a number of unidentified peaks. The significant number of these peaks demonstrates the complex composition of APM, especially considering that our methodology only allows for the analysis of acids detectable by UV–vis absorption. Phthalic acid was the predominant species present, with typical concentrations ranging from 5 to 30 ng/m^3. The abundance of ACOAs in the samples studied was in general agreement with previous results reported by other groups (3,5,9). To our knowledge, 4-nitrophenol has only been identified in ambient samples collected in Yokohama, Japan (24) as well as in smog chamber experiments from the oxidation of aromatic hydrocarbon precursors (2). In the former reference, six other nitro- and methylnitrophenols were identified as components of APM; however, we found them to be absent from all of our samples. In addition, the analysis of samples collected inside the Union Station overpass showed the presence of all compounds detected in ambient samples at raised concentrations (ranging from 3 times for *o*-phthalate to 30 times for 4-hydroxybenzoate), indicating that they were (at least partly) of primary anthropogenic origin. Furthermore, 3-hydroxyphthalic acid was also identified in these vehicle emission studies, which to our knowledge has not been reported as a component of APM.

Conclusion

In this work, a method for the determination of ACOAs and nitrophenols in APM has been developed. The separation method using an 11% acetonitrile–20mM borate (pH 9.9) buffer provided an adequate resolution of APM-derived ACOAs and nitrophenols. Migration time reproducibility was generally better than 1.5%, and day-to-day repeatability was always under 3%. Detection limits were in the order of 40 to 130 ng/mL. In light of the complex composition of atmospheric particulate samples, spectral information from the photodiode array employed in this study proved indispensable for peak purity evaluation. The ACOAs and nitrophenols studied in this work were generally present in atmospheric aerosols at low concentrations (an extraction method using HCl and diethyl ether was employed to allow their detection and quantitation). A preconcentration factor of up to 100 can be achieved with this protocol. Recoveries of spiked standards ranged from 59% to 102%, with RSD values between 2% and 17% for five extractions. The extraction method is inexpensive, and can be performed in less than 3 h, which is adequate. The disadvantage of this CE method versus existing GC–MS protocols for similar applications is that it does not allow for the

analysis of as wide a range of compounds in a single run. However, the advantages of short analysis time, ease, and low cost inherent in CE make it a valuable complement to the already existing GC–MS protocols, allowing one to study specific classes of acids in the complex matrices of atmospheric aerosols.

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