Measurements of Low-Molecular-Mass Carboxylic Acids in Atmospheric Aerosols by Capillary Electrophoresis

Shidong Gao and **Jochen Rudolph***

Department of Chemistry, Centre for Atmospheric Chemistry, York University, 4700 Keele Street, Toronto, Ontario, M3J 1P3, Canada

Abstract

Capillary electrophoresis (CE) methods for the determination of low-molecular-mass (LMM) carboxylic acids in airborne particular matter have been developed. The separations of 22 LMM carboxylic acids, including acids derived from the oxidation of biogenic hydrocarbons, are performed using a background electrolyte consisting of 3.0mM 2,6-naphthalenedicarboxylic acid and 18.0mM 2,2-bis (hydroxymethyl)-2,2',2"-nitrilotriethanol (Bis-tris) in 16% (v/v) 1-propanol within 10 min. Using a combination of a buffer mixed with an organic solvent and electroosmotic flow modifier, a minimum of peak overlaps is achieved with migration time variation of less than 1% and peak area ratio (relative to an internal standard) variation of less than 5% within 1 day. The detection limits for the aliphatic LMM acids that can be determined by this method are in the range of 30–140 µg/L. Furthermore, a simple method for efficient extraction of LMM organic acids from particulate atmospheric matter collected on quartz fiber filters using high-volume samplers is developed. Combining the extraction procedure with a reduction of the extract to approximately 0.2 mL allows for the measurement of LLM in atmospheric particulate organic matter at concentrations well below 1 ng.m^{-3}. Repeat analysis of filters collected in tunnels, urban, suburban, and forested areas demonstrate that the procedure allows for measurements of aliphatic and aromatic LMM acids within a variability of 10–25%.

Introduction

In recent years the analysis of low-molecular-weight organic acids (LMM) in atmospheric particulate matter (PM) has become more and more important. Consequently there is a substantial number of analytical techniques (1,2), mostly based on chromatographic methods such as ion chromatography, gas chromatography (GC), and high-performance liquid chromatography (HPLC). Capillary electrophoresis (CE) has also recently been employed to analyze the most abundant organic acids such as oxalic, formic, acetic, and malonic acids in PM (3–6).

However, only a few methods using CE to determine more complex organic acids in the atmosphere have been published.

The main reason for this is the low abundance of many of these LMM in the atmosphere [e.g., measurements of pinic and norpinic acid by GC–MS showed that their concentration in the atmosphere is in the range of several ng.m^{-3} and less (7)]. Another problem is the presence of a large excess of inorganic ions and nonionic organic material in atmospheric PM.

In this study an optimized procedure for measurement of a broad range of organic acids in atmospheric PM by CE is presented. The procedure is the result of modifications of existing CE methods using direct UV–vis detection for phenols and aromatic acids (8) and indirect detection for aliphatic acids (3) and can be combined with a very simple extraction and sample preparation procedure.

Experimental

Reagents and buffers

All chemicals were of analytical grade and were purchased from Sigma-Aldrich (Ontario, Canada) without further purification. Stock solutions of organic acids (500–1000 µg/mL) for preparation of standard mixtures were prepared by dissolving appropriate amounts of acid 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 polytetrafluoroethylene (PTFE) filters (Chromatographic Specialties, Ontario, Canada).

Stock buffer mixtures had a concentration of 5.0mM 2,6-naphthalenedicarboxylicacid (NDC), and 30mM 2,2Bis (hydroxymethyl) 2,2',2"-nitrilotriethanol (Bis-Tris). The stock buffer solution was prepared weekly. A run buffer solution was prepared daily by diluting the stock solution with the appropriate amounts of organic solvent and deionized water. The pH of the buffer solutions was measured, but not adjusted. Table I shows the composition of the different buffers. All buffer solutions were filtered through 0.45-µm PTFE filters and then degassed in an ultrasonic bath for 20 min prior to usage.

Instrumentation

Determination of LMM aliphatic and alicyclic acids were performed on a Beckman P/ACE System MDQ instrument (Fullerton, CA) using the commercial standard software for the data acquisition and processing. The CE fused-silica capillaries

* Author to whom correspondence should be addressed: email rudolphj@yorku.ca.

had an inside diameter of 100 µm and a total length of 62.5 cm (52 cm to the detector). A 100- × 800-µm detector aperture was used in the diode array UV–vis detection system. The capillary temperature was controlled at 293 K. The electrophoretic separations were conducted under reversed polarity. Electropherograms were determined by monitoring absorption at 244 nm with a bandwidth of 6 nm using a data acquisition rate of 4 Hz. The signals were inverted in order to convert the electropherograms with the negative peaks resulting from indirect detection into conventional "positive" signals.

Measurements of aromatic acids were performed on a Hewlett-Packard 3D-CE instrument (Waldbronn, Germany) equipped with a photodiode array detector and buffer replenishment system using Hewlett Packard Capillary Electrophoresis software (revision 6.1) for data acquisition and processing. Details of the procedure were described by Rudolph and Stupak (8).

Separation conditions

New capillaries were flushed with methanol (10 min), deionized water (5 min), 1M HCl (10 min), deionized water (5 min), 1M NaOH (10 min), and water (5 min). Prior to each usage, the capillaries were conditioned by flushing with 1.0M NaOH (2 min), 0.2M NaOH (10 min), water (5 min), and the run buffer (15 min). Finally a voltage of –30 kV was applied for 15 min. In case of using hexadimethrine bromide (HDB) as the modifier, the capillary was flushed with the HDB-containing buffer solution (buffer 1, composition see Table I) for 1 min, followed by HDB-free separation buffer solution (buffer 2) for 10 min before applying a voltage of –30 kV for 15 min. Between the runs the capillaries were flushed with buffer 2 for 0.5 min, followed by buffer 1 for 1 min and then again with buffer 2 for 1.5 min. At the end of each day, the capillary was rinsed with 0.2M NaOH (5 min), deionized water (5 min), and flushed with air for 3 min.

Typically the samples were injected into the capillary hydrodynamically, applying a pressure of 0.5 psi for 10 s. In some cases pressure or duration of injection was modified or samples were injected electrokinetically by applying a voltage of –10 kV for 10 s. In most cases the separation voltage was –30 kV, but for several tests lower separation voltages were used.

Sampling and sample preparation

Airborne PM was collected on 8" × 10" Quartz fiber filters (Pallflex Products, Putnam, CT) using Hi-Vol air samplers. Average flow rates were 1.13 m³/min, and typically samples were collected for 24 h. Prior to sampling, new filters were baked at 750°C for 24 h. After sampling, the filters were divided into eight parts and stored at –20°C in gas-tight glass jars under a nitrogen

atmosphere. For all extractions 1 of these ⅛ pieces of filter was used.

After addition of 16 µg 1-octanesulfonic acid and 4 µg p-methoxy benzoic acid as internal standards, the quartz fiber filter was extracted by 10 mL HPLC-grade methanol in an ultrasonic bath for 15 min. After removing the methanol extract the quartz fiber filter was rinsed twice with 2 mL of methanol. The rinse solutions and extract were combined and syringe filtered with a 0.45-µm hydrophilic polypropylene filter. After the addition of 20 µL 1mM NaOH, the volume of the solution was reduced to approximately 1.0 mL under a stream of pure nitrogen gas, 0.5 mL water was added, and then the solution was reduced to 200 µL. Prior to CE analysis, the concentrated extracts were filtered through a 0.45-µm pore diameter PTFE filter.

A Dionex ASE 200 accelerated solvent extractor (ASE) (Dionex Canada, Ontario, Canada) was used for validation of the extraction method. The functional components and operating principles of the ASE have been described by Richter et al. (9). The procedure used here closely followed a method for analysis of polycyclic aromatic hydrocarbons in atmospheric PM (10). Briefly, the extraction procedure uses organic solvents at high pressures and temperatures above the ambient pressure boiling point. After the addition of internal standards, the filter was enclosed in a stainless steel cell, which was then filled with methanol and statically extracted at 423 K and 1500 psi for 7 min.

Results and Discussion

Separation conditions

The separation conditions were optimized using artificial mixtures containing 2 mg/L of each of the 22 aliphatic and 18 aromatic compounds. The mixtures also contained 50 mg/L of chloride, sulfate, and nitrate to simulate the presence of large amounts of inorganic ions in atmospheric PM. An example of an optimized separation of the 22 aliphatic acids in the test mixture is shown in Figure 1, and an example for the separation of an extract of atmospheric PM is shown in Figure 2. It should be noted that the analysis of oxalate is not possible in the presence of an extreme excess of inorganic ions, but dilution of the sample or injection of smaller samples resolved this problem (see below). There are a considerable number of separation parameters that influence the separation and had to be optimized to achieve necessary completeness of the separation. The following part of this section will briefly discuss the most important optimization steps.

Variations of the type and concentration of the electroosmotic flow (EOF) modifier mainly served the purpose of finding a compromise between the duration of the CE separation and the width of the retention time window available for analysis of the target compounds. The flow modifiers tested were the widely used long-chain alkyltrimethylammonium salts, such as cetyltrimethylammonium bromide (CTAB) (11,12), tetradecyltrimethylammonium bromide (TTAB) (3), and HDB (6,13). Characterizations of different cationic surfactants for the analysis of inorganic anions and below-C_4 carboxylic acids have been reported (14–16). Under the experimental conditions the EOF mobilities for CTAB, TTAB, and HDB were 6.4×10^{-5}, 9.7×10^{-5}, and 5.9×10^{-5} cm²/s/V, respectively. For the aliphatic LMM

Table I. Composition of Buffer Solutions

Buffer solution	Bis-tris (mM)	CTAB (mM)	HDB	TTAB (mM)	NDC (mM)	1-Propanol	pH
CTAB-buffer	14.5	0.10	–	–	4.0	–	5.86
HDB-buffer 1	18.0	–	0.001% (w/v)	–	3.0	16% (v/v)	6.00
HDB-buffer 2	18.0	–	–	–	3.0	16% (v/v)	6.00
TTAB-buffer	14.5	–	–	0.16	4.0	–	5.86

studied here, the electrophoretic mobilities of the organic ions did not significantly change among the three EOF modifiers, except pinonate. Changing from HDB to CTAB decreased the electrophoretic mobility of pinonate from 2.3×10^{-4} cm^2/s/V to 1.6×10^{-4} cm^2/s/V, which was most likely the consequence of the formation of weak complexes between CTAB and pinonate.

We therefore decided to use HDB, an alkylammonium polymer composed of hexadimethylammonium (25–50) units. Its very effective adsorption at the capillary wall allows for modifying the capillary walls prior to the CE separation and running the separation using a buffer without flow modifiers. This minimizes possible interferences caused by the formation of insoluble pairs between alkylammonium ions and electrolyte or sample components (14).

It has been reported that the addition of organic solvents such as aliphatic alcohols or acetonitrile to the separation buffer has a substantial impact on the electrophoretic mobility of aromatic acids and phenols (8,17,18). This is also observed for the LMM acids studied here (Figure 3). The smallest effect is seen for acetonitrile, and the largest is for *n*-propanol. Similarly, the effect increases with increasing concentration of the solvent. Generally, the electrophoretic mobilities at different solvent concentrations and for different types of solvent are highly correlated, with linear correlation coefficients (R^2) exceeding 0.99. This indicates that the main impact of the addition of organic solvents on the electrophoretic mobility of LMM is attributable to changes in buffer viscosity. This is supported by the observation that the EOF closely follows the changes in electrophoretic mobility (Figure 3). Nevertheless, for some of the LMM (e.g., glycolate, acetate, and benzoate), small deviations from this strict linear dependence are observed, which allows further optimization of the separation by changing the concentration and type of the organic solvent. The best results were obtained with a concentration of 16% (v/v) *n*-propanol in the buffer. This relatively high concentration of organic modifier has the additional benefit of reducing the electric conductivity of the buffer, which allowed using a separation voltage of –30 kV in combination with a 100-μm-diameter CE column.

A specific problem is the separation between oxalate and the inorganic ions. Both in extracts of ambient PM samples and in the test mixtures, the overlap with inorganic ions, which are present in large excess, make the evaluation of the oxalate peak problematic. Tests conducted with varying concentrations of inorganic ions showed that a sufficient resolution for oxalate can be achieved if the total amount of inorganic ions injected is below 2 ng. For ambient samples, dilution of the PM extract by a factor of 8 or injection of only a very small sample volume of 5 nL instead of the 47.5-nL samples used for the analysis of the other LMM allowed quantitative evaluation of oxalate. The results obtained for oxalate by both methods agreed with each other within better than ± 10%.

Reproducibility, detection limits, and linearity

The repeatability and reproducibility of migration time was determined by repeat measurements of a mixture of standards at concentrations in the range 1–8 mg/L over 3 months using 3 different capillaries. The relative standard deviations of intraday (< 1.0%) were usually smaller than those of day-to-day (< 5.0%) variability of the retention times. The intraday relative standard deviations of peak area and peak area ratio (relative to an internal standard) was less than 5%. The long-term precision of peak area ratios over 3 months using 3 different capillaries ranged from 7.3% to 15.7% for the studied concentration range. The highest variability was found for oxalate, most likely due to the problematic separation between oxalate and the inorganic ions.

The detection limits (95% confidence limit) for the acids were in the range of 30–140 μg/L when using a 10-s × 0.5-psi injection
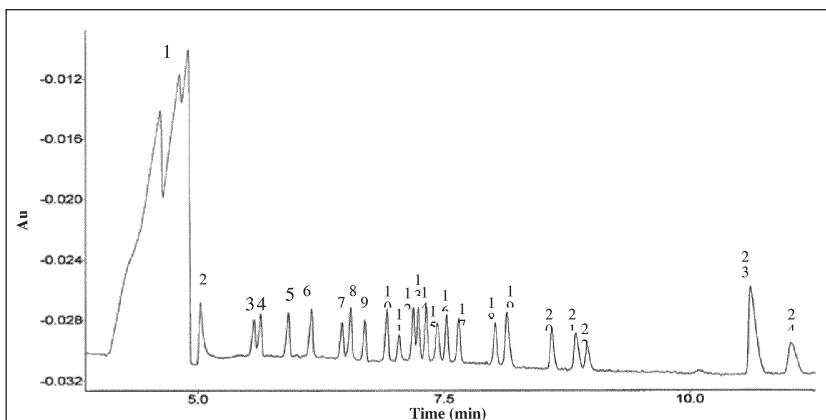
Figure 1. Separation of artificial mixture of LMM aliphatic and alicyclic acids. Separation conditions: run buffer with 3.0mM NDC, 18.0mM Bis-tris, and 16% (v/v) 1-propanol (pH 6.00); conditioning of capillary with 0.001% HDB (w/v); sample injection, 0.5 psi × 10 s; separation voltage, –30 kV; indirect UV detection, 244 nm; and capillary temperature, 20°C. Peak identities (each 2 mg/L unless given otherwise): inorganic ions Cl⁻, NO₃⁻, SO₄²⁻ (each 50 mg/L) (1); oxalate (4 mg/L) (2); malonate (3); formate (4); malate (5); succinate (6); methanesulfonate (7); glutarate (8); *o*-phthalate (9); adipate (10); pyruvate (11); glycolate (12); pimelate (13); acetate (14); norpinate (15); suberate (16); pinate (17); lactate (18); propionate (19); 2-hydroxy butyrate (20); butyrate (21); benzoate (22); 1-octane sulfonate (internal standard) (23); and pinonate (4 mg/L) (24).
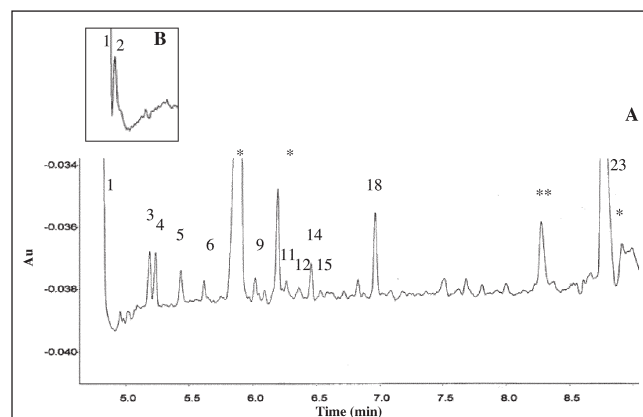
Figure 2. Example of capillary electropherogram of an extract of atmospheric PM collected on a quartz fiber filter. Experimental conditions and peak identity as described in Figure 1; unknown peaks (*); and internal standard for aromatic acids analysis (**). Extract without dilution (A) and oxalate analysis with extract diluted by a factor 8 (B).

(Table II). The detection limits were least favorable for oxalate and pyruvate. As expected, an increase in size of the injected sample increased sensitivity. Changing the injection from 3-s × 0.5-psi (47.5 nL injection volume) to 20-s × 0.5-psi (316 nL injection volume) substantially reduced the detection limits for the 22 acids. However, this also increased the peak width and resolution between formate and malonate, and glycolate and pimelate and butyrate and benzoate decreased to less than 1.

It has been reported that electrokinetic injection allows better detection limits for measurements of aliphatic LMM acids than pressure injection (3). However, the detection limits achievable by electrokinetic injection highly depends on the concentration of inorganic ions in the sample. For samples containing 10 mg/L of Cl^-, NO_3^-, SO_4^{2-} each, the detection limits achieved by electrokinetic injection are approximately equal to those using pressure injection (Table II). Only at lower concentrations of inorganic ions will electrokinetic injection allow lower detection limits than pressure injection.

Linearity was investigated by analyzing mixtures of standards at concentrations in the range of 1–8 mg/L using 0.5-psi × 10-s pressure injection, and in the range of 0.5–6 mg/L using –10-kV × 10-s electrokinetic injection. The coefficients of correlation for a linear dependence between peak area and concentration were better than 0.998 for all of the 22 studied organic acids.

Extraction efficiency

The efficiency of the extraction procedure was tested by spiking clean quartz fiber filters with defined amounts of the target analytes and subsequent analysis of these filters following the described procedure. A comparison of the extraction efficiencies for different solvents is given in Figure 4 for LMM aliphatic (Figure 4A) and aromatic (Figure 4B) acids. Methanol was chosen for the extraction. The extraction efficiencies when using methanol were close to 100% and subsequent reduction of
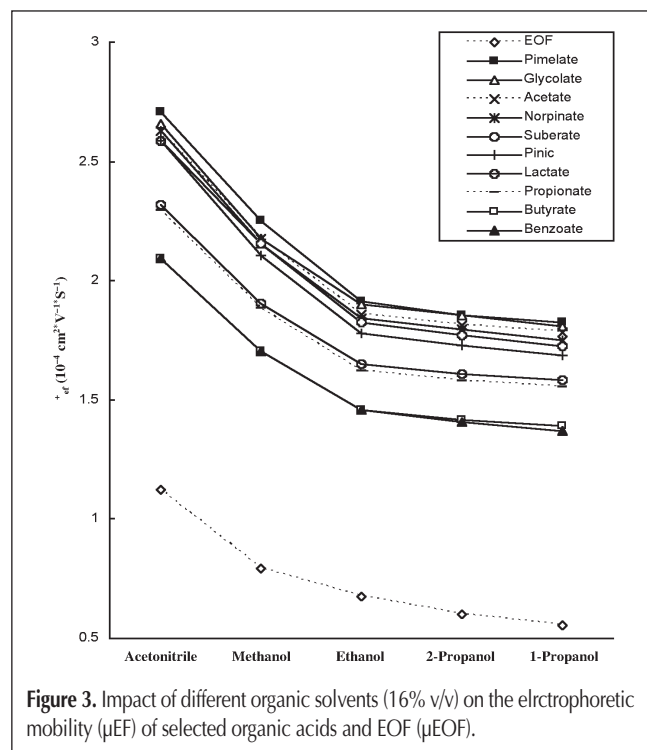
Table II. Detection Limits for LMM Organic Acids		
	DL* (µg/L)	
Analyte	Electrokinetic injection	Pressure injection
Oxalate	89	128
Malonate	46	70
Formate	24	24
Malate	42	53
Succinate	55	54
Methane sulfonic acid	40	101
Glutarate	80	81
o-Phthalate	66	56
Adipate	81	84
Pyruvate	82	140
Glycolate	40	46
Pimelate	84	72
Acetate	83	28
Norpinate	45	97
Suberate	74	69
Pinate	83	48
Lactate	66	97
Propionate	39	63
2-Hydroxy butyrate	52	30
Butyrate	67	87
Benzoate	75	75
Pinonate	69	49

* Calculated for a 95% confidence level (DL = tn – 1S, where S is standard deviation).
† Determined using electrokinetic injection (–10 kV × 10 s) in the presence of 10 mg/L Cl^-, NO_3^-, and SO_4^{2-}.
‡ Injection: 0.5 psi × 10 s.

Figure 3. Impact of different organic solvents (16% v/v) on the elrctrophoretic mobility (µEF) of selected organic acids and EOF (µEOF).
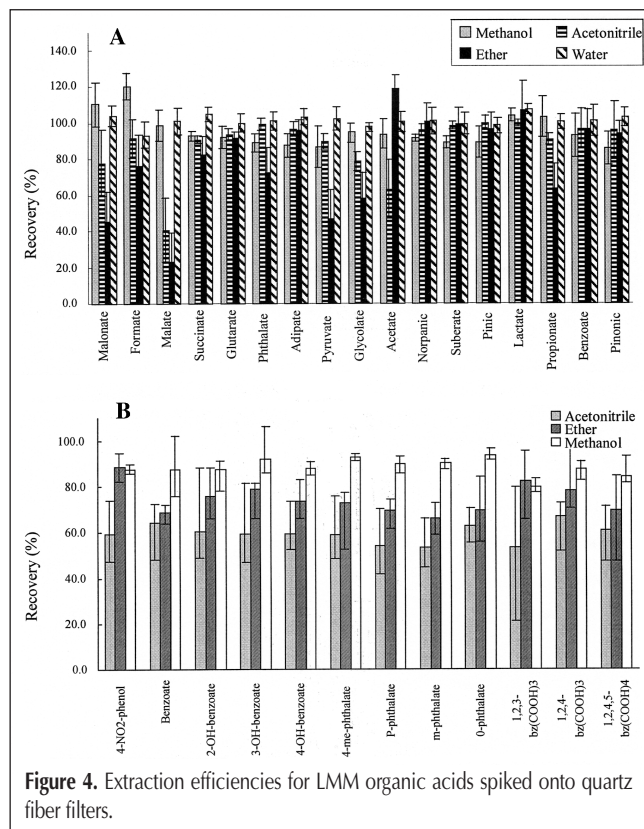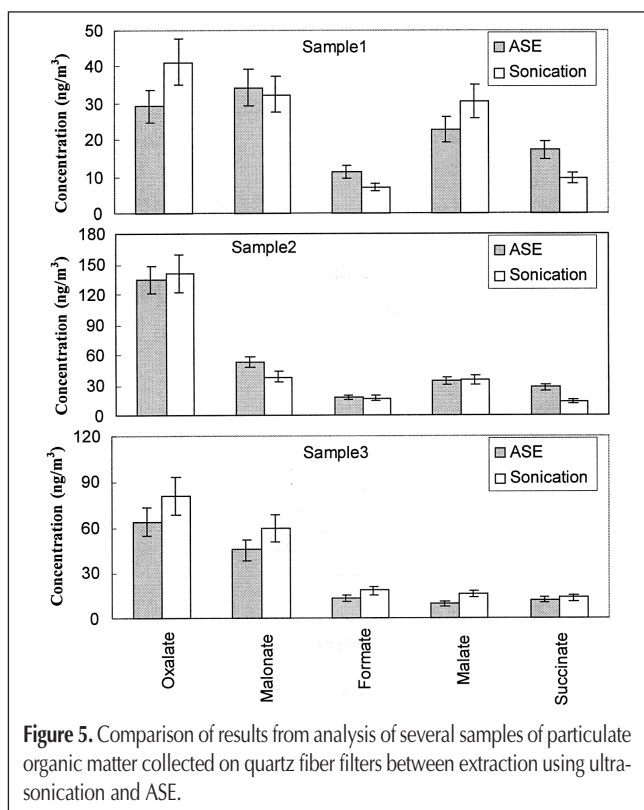

Figure 4. Extraction efficiencies for LMM organic acids spiked onto quartz fiber filters.

volume can be conducted efficiently at room temperature, minimizing the risk of sample degradation.

Currently, soxhlet extraction, ultrasonication, ASE, or shaking are widely used for extraction of atmospheric PM collected on filters. It has been reported that ultrasonication, although an efficient and widely used method, can induce or accelerate chemical reactions, which may result in a pronounced change of the measured concentration of some chemical species when ultrasonication is used for more than 15 min (19). Therefore, a comparison between this procedure, which is based on ultrasonication, and ASE was conducted. The results obtained for ambient samples (Figure 5) show no significant or systematic differences among the different extraction methods.

Analysis of atmospheric PM samples

Typically, the air volume sampled by high-volume particle samplers during a 24-h period is approximately 1600 m^3. Based on the extraction efficiencies, the size of the filter segments (1/8 pieces) extracted by this procedure, and the final volume (0.2 mL) of the concentrated sample, the overall detection limits in air could be calculated from the detection limits of the CE analysis and, where applicable, variability of the blank values. Blank values were found for formate, acetate, lactate, and benzoate. For none of the other compounds could a signal exceeding the detection limit be found in the extracts of blank filters. For the LMM aliphatic acids with detectable blank values the detection limits in atmospheric PM range from 0.03–0.1 ng/m^3, for aromatic LMM acids, which can be determined by direct UV–vis adsorption, the detection limits are even lower (8). For compounds with detectable blank values the detection limits are less favorable, ranging from approximately 1–2 ng/m^3 for formate, acetate, and benzoate to approximately 5 ng/m^3 for lactate.

Figure 5. Comparison of results from analysis of several samples of particulate organic matter collected on quartz fiber filters between extraction using ultrasonication and ASE.

The ambient concentration of the LMM acids we found in continental air over Canada range typically between 10 ng/m^3 and 1 ng/m^3 for the most abundant acids such as oxalate, malonate, malate, succinate, and pyruvate, and from a few ng/m^3 to a fraction of a ng/m^3 for less abundant LMM acids such as glutarate, subarate, pinate, norpinate, and most of the aromatic acids. These concentrations are generally above our detection limit and consequently in most ambient samples the LMM acids could be identified and their concentrations quantitated by comparison with standard solutions.

For the measurements of aliphatic LMM acids, one also must consider the uncertainties in peak identification and the possibility of peak overlaps, a consequence of the lack of selectivity when using indirect UV–vis detection. Indeed, based on a comparison of retention time and peak width between standards and samples, it was found that methanesulfonate, glutarate, adipate, and pinonate in some samples overlapped with peaks of unknown compounds. Because for indirect detection the migration time is the only information available for peak identification, the problem of unidentified peak overlaps can only be treated as a statistical problem. The 22 aliphatic LMM acids analyzed here are those expected to be present in ambient PM samples. Nevertheless, this does not exclude overlap with unknown compounds. Indeed, the electropherograms of ambient samples contain a number of unidentified peaks (e.g., Figure 2), although most of these peaks are very small compared with the peaks of the target compounds. Based on this, it was concluded that the number of major unidentified peaks is only small. Because the peak capacity of the relevant migration time window in which the 22 identified compounds elute is close to 80, a complete overlap of one of the target compounds with a major unknown peak (which would not result in detectable peak broadening or shoulders) is unlikely but not entirely impossible. Overlaps with very small unidentified peaks have a higher probability, due to the considerable number of unidentified very small peaks. However, because these peaks are small compared with the peaks of the target LMM acids, a resulting bias generally will be within the estimated uncertainty of the measurements.

Apart from these overlaps and concentrations close to the lower limit of detection, the reproducibility of the measurements was in the range of 10–25%. This reproducibility was derived from comparison of 46 pairs of repeat analysis of two different segments of the quartz fiber filters. These 46 pairs were randomly selected and therefore covered a wide range of different levels of concentrations of LMM organic acids in atmospheric particulate. (e.g., the average concentrations for malonate ranged from 25 ng/m^3 in forest samples to 140 ng/m^3 in tunnel samples).

Conclusion

A reliable and economic method for CE analysis for LMM acids has been developed. This CE method is suitable for the analysis of the concentrated extracts of PM collected on quartz fiber filters by high-volume samplers. The CE method allows analysis of the concentrated extracts without any further clean-up procedure. Except for oxalate, the presence of a large excess of inorganic ions

and nonionic organic material had no adverse effect on the measurement of the LMM acids. The problem of interference between oxalate and the inorganic ions can be resolved by injecting smaller or diluted samples. The extra effort of an additional CE analysis is considerably lower than any sample clean-up procedure, which would also add additional risk for losses or contaminations. The advantage of a simple extraction and sample concentration procedure is also obvious from the marginal impact of blank values. With the exception of formate, acetate, lactate, and benzoate, no blank values were found for the 40 LMM acids analyzed.

Using filter samples from high-volume samplers, detection limits for most of LMM acids in ambient PM were below 0.1 ng/m^3, when sampling for 24 h, which is sufficient for nearly all applications. Similarly, the reproducibility, which was in the range of 10–25%, and the linear range of the method were suitable for measurements of LMM acids in PM in air for a wide range of pollution levels.

The most serious drawback of the method is the lack of selectivity for the detection of aliphatic LMM acids. The consequence of using indirect detection is that peak identification and the absence of overlaps depends entirely on retention time and peak width. Clearly, the high intraday reproducibility of this method reduces the risk of incorrect peak identification and is also very valuable for discovering peak overlaps. Based on probability considerations, it was concluded that major unrecognized peak overlaps were unlikely. However, overlaps with minor peaks could not be excluded. Based on these considerations, it was concluded that this method would give reliable results for concentrations well above the lower limit of detection, whereas for concentrations close to the detection limit, bias due to peak overlaps could not be ruled out.

Acknowledgments

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