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Capillary electrophoretic separation of dicarboxylic acids in atmospheric aerosol particles

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Abstract

2,3-Pyrazinedicarboxylic acid (PZDA), 2,6-pyridinedicarboxylic acid (PDA) and 2,3-pyridinedicarboxylic acid (QUIN) solutions were studied as background electrolytes (BGEs) in the capillary electrophoretic analysis of dicarboxylic acids in aerosol particles with indirect UV detection. The BGEs were selected on the basis of similarity in structure with the analytes so that mobilities would be compatible. Optimised pH values for PZDA, PDA and QUIN solutions were 10.6, 11.0 and 10.2, respectively. Myristyltrimethylammonium hydroxide and myristyltrimethylammonium bromide were added to reverse the electroosmotic flow in the solutions in the direction of anode to enable fast anion detection. Separation was obtained for nine dicarboxylic acids (C_2–C_{10}) differing in the number of CH_2 groups in their skeleton. The electrophoretic mobilities were determined to lie in the range 3.0×10^{-4}–7.0×10^{-4} $cm^2\ V^{-1}\ s^{-1}$. The relative standard deviations (RSDs) for the absolute migration times of the analytes were mostly less than 0.5% ($n=6$) in PZDA solution. In PDA solution the within-day and day-to-day RSD values for migration were less than 1% and between 2 and 4%, respectively. Peak heights and areas mostly deviated between 1 and 15% in both PZDA and PDA solutions. Detection limits ranged between 1 and 5 mg/l. Methods were applied to the analysis of dicarboxylic acids isolated from aerosol particles.

Keywords: Aerosol; Air analysis; Background electrolyte composition; Environmental analysis; Dicarboxylic acids; Carboxylic acids

1. Introduction

Atmospheric aerosol particles play an important role in climate and atmospheric chemistry [1]. Aerosol particles affect human health and participate in climate interactions, acid precipitation and visible reduction on the globe [2].

Aerosol properties, like the capability of particles to form water droplets at atmospheric supersaturation levels, are measured by the particle size, chemical composition and surfactant characteristics [3,4]. The cloud droplet activation properties of water-soluble inorganic aerosols have been particularly well studied [4], and the anthropogenic influences on sulphate, nitrate, chloride as well as trace metal concentrations are documented [5]. The study of organic aerosols and their composition is essential to an understanding of a diversity of processes in the atmosphere, including solar radiation scattering, con-

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densation in cloud formation oxidation processes and new particle formation. Only, minor attention has been focused on the nucleation of organic aerosols, most probably because of poor knowledge of the organic matter, which typically contains vast numbers of organic compounds in low concentrations. Modern analytical instruments are needed for the identification of organic compounds in aerosols [6,7].

Dicarboxylic acids (DCAs) and monocarboxylic acids (MCAs) have been identified as the major constituents of organic aerosols. Because of the key role DCAs play in nucleation processes, they are of great interest in the chemical characterization of the atmosphere [8]. Organic acids participate in the gas-to-particle conversion and they can act as cloud condensation nuclei [9]. Great interest has already been focused on the role of MCAs, particularly formic and acetic acids, in the troposphere [10,11]. Khwaja [5] showed that formic acid and acetic acid are present in the atmosphere mostly in gaseous form with less than 10% in the particle phase. DCAs, on the other hand, exist mainly in the particle phase because of their low vapour pressures. In a semi-urban site in the USA, oxalic acid was found to be the most abundant DCA, followed by succinic acid and malonic acid. Limbeck and Puxbaum [8] found that oxalic, malonic and succinic acids were the dominant compounds in aerosol samples, and Kavouras et al. [12] detected oxalic, formic, acetic, lactic and propanoic acids in an air sample.

The presence of DCAs in aerosols may result either from primary emissions or from secondary photochemical reactions [9]. The common and widespread non-methane hydrocarbons emitted by vegetation are suggested as the possible precursors [13,14]. In addition, studies related to gaseous and particulate atmospheric species from a forested area have shown that terpenes emitted by vegetation are photo-oxidized to organic acids, such as pinonic acids, and condensed to form organic aerosols [12].

Organic ions in environmental samples are usually studied by high-performance liquid chromatography (HPLC), ion chromatography (IC), gas chromatography (GC) with and without derivatization, or capillary electrophoresis (CE) with indirect UV detection [5,8,14]. One drawback to the chromatographic techniques is that extended sample pre-treatment and relatively long analysis times are required to obtain the separation efficiency good enough for quantification [15]. CE techniques with high separation efficiencies have recently been used in the analysis of anions in atmospheric aerosols and environmental water samples [15–18].

The purpose of our study was to develop and optimise capillary electrophoresis methods based on indirect UV detection for the quantitative analysis of organic dicarboxylic acids in aerosol samples containing large amounts of inorganic and organic ions. The methods were compared in terms of accuracy, reliability and sensitivity. Since most organic anions have little or no UV absorbance, search was made for a good chromophore for the background electrolyte solution. The background electrolyte (BGE) has a marked effect on the sensitivity of the detection. The mobilities of analytes and the BGE should match to ensure good separation and sensitivity. In addition, the aerosol particles should not contain the compounds of the BGE solution. Modifiers were used in the BGE to reverse the direction of electroosmotic flow (EOF) to allow fast analysis of small-sized anions.

2. Experimental

2.1. Instrumentation

A Hewlett-Packard ^{3D}CE System (Agilent Technologies, Waldbronn, Germany) equipped with a photodiode array UV detector was used for the optimisation and a Beckman P/ACE MDQ capillary electrophoresis system (Beckman-Coulter Instruments, Fullerton, CA, USA) with a photodiode array UV detector for the analysis of the real aerosol samples. The UV wavelength range that was studied was from 190 to 400 nm. The fused-silica capillaries (Composite Metal Services, The Chase, UK) were 58.5 cm (effective length 50 cm)×50 μm I.D.×375 μm O.D. The applied voltage varied from −20 to −24 kV [−21 kV for 2,3-pyrazinedicarboxylic acid (PZDA), −24 kV for 2,6-pyridinedicarboxylic acid (PDA) and −20 kV for 2,3-pyridinedicarboxylic acid (QUIN)]. Samples were injected with a pressure of 50 mbar for 6 s for the optimisation (HP) and 2 p.s.i. (1 p.s.i.=6894.76 Pa) for 6 s in the analysis of the

real samples (Beckman). The temperature was maintained at +25 °C during the analyses.

A Meter Lab PHM 220 laboratory pH meter (Radiometer, Copenhagen, Denmark) was used for the pH measurements. The combination electrode was calibrated with standard solutions of pH 4.00, 7.00 and 10.00 manufactured by Merck (Darmstadt, Germany).

2.2. Chemicals

Oxalic acid ($C_2O_4H_2$, purity 99%, pK_{a1} 1.27, pK_{a2} 4.27), malonic acid ($C_3O_4H_4$, purity 99%, pK_{a1} 2.85, pK_{a2} 5.70), succinic acid ($C_4O_4H_6$, purity 99%, pK_{a1} 4.21, pK_{a2} 5.64), glutaric acid ($C_5O_4H_8$, purity 99%, pK_{a1} 4.32, pK_{a2} 5.42), adipic acid ($C_6O_4H_{10}$, purity 99%, pK_{a1} 4.41, pK_{a2} 5.41), pimelic acid ($C_7O_4H_{12}$, purity 98%), suberic acid ($C_8O_4H_{14}$, purity 98%), azelaic acid ($C_9O_4H_{16}$, purity 98%), sebacic acid ($C_{10}O_4H_{18}$, purity 99%), myristyltrimethylammonium bromide (MTAB), QUIN, PZDA and PDA were purchased from Sigma–Aldrich (Steinheim, Germany) [19]. OFM Anion BT (myristyltrimethylammonium hydroxide, MTAH) was from Waters (Milford, USA). NaOH solutions (0.1 and 1.0 *M*) were manufactured by Merck and HPLC-grade methanol was from J.T. Baker (Deventer, The Netherlands).

Before use the electrolyte solutions were filtered through Gelman Acrodisc CR PTFE syringe filters (13 CR, 0.45 μm, Gelman Sciences, Ann Arbor, MI, USA) and degassed by ultrasonication. Distilled water was deionised (18 mΩ cm^{-1} at 25 °C) before use with a Milli-Q apparatus (Millipore, Molsheim, France).

2.3. Background electrolyte solutions

Three electrolytes, prepared of QUIN (pK_{a2} 1.90), PDA (pK_{a2} 1.20) or PZDA (pK_{a2} 4.12), were tested during this work. The pH during the optimisations was between 7 and 13, which ensured full ionisation of both the analytes and BGEs. The concentration of the BGEs was varied between 1 and 20 m*M* during the optimisations. All three BGEs (QUIN, PDA and PZDA) also worked as chromophores, a necessary feature owing to the lack of UV absorbance of the analytes. Thus, indirect UV detection was applied. The PZDA electrolyte solution also contained MTAH, while the PDA and QUIN solutions contained MTAB as a modifier. Modifiers reverse the direction of the EOF and move the anions in the same direction, towards the positive detector end of the capillary. Different compositions of the BGEs were tested to optimise the separation. The best sensitivity for most analytes was achieved with the PZDA electrolyte, and it was used as the main electrolyte in further studies. Results obtained with the optimised system were compared with results obtained with the PDA electrolyte.

A stock solution (25 mmol/l) of each electrolyte was prepared in water and stored at +4 °C. The stock solutions were diluted to working concentrations immediately before analysis. The pH adjustment was made, with 1.0 and 0.1 *M* NaOH, just before the filtration of the electrolyte before use.

2.4. Conditioning of the capillary

Before first use the capillary was rinsed with 0.1 *M* NaOH, water and BGE for 15 min each. Before each injection the capillary was flushed with electrolyte solution for 2 min to keep the migration times of the analytes repeatable.

Migration times were more repeatable when the capillary was flushed with electrolyte solution between runs rather than with NaOH. This is in agreement with the studies of Ehmann et al. [19]. An electroconditioning step (2 min, −15 μA) between the analyses was tested and it did not improve the repeatability significantly.

2.5. Standard mixtures

Stock solutions (1000 mg/l) of each dicarboxylic acid separately and a mixture of all nine (9000 mg/l) were prepared in MeOH. The stock solutions were stored at −20 °C. Optimum conditions for the different electrolyte solutions were sought with the use of a 10 mg/l mixture prepared from the stock solution mixture. In the linearity studies the DCA stock solutions were diluted with methanol to concentrations of 1 to 100 mg/l before use.

2.6. Aerosol particle samples

The aerosol particle samples were collected from the Helsinki area during April and May 2002. The collection was made on 47 mm Whatman QM-A quartz microfibre filters (Whatman, Maidstone, UK) at a flow-rate of 20.5 l/min for 48–72 h. Before use, the filters were preheated to 500 °C for 10 h to remove organic contaminants. Masses of the filters were measured before and after the sampling. The filters were kept at room temperature in a desiccator for 2 days before the measurements. Analytes were extracted from the filters with 5 ml of Milli-Q water and ultrasonicated for 20 min. Extracts were stored at +4 °C until the analyses were made.

3. Results and discussion

3.1. Optimisations

Three BGE solutions containing UV-absorbing PDZA, PDA and QUIN were tested in a search for optimal conditions for the determination of DCAs in atmospheric aerosol particles by capillary electrophoresis with indirect UV detection. The performance of the BGE solutions at basic pH was evaluated in terms of BGE concentration, pH, counter-ions and the myristyltrimethylammonium (MTA) ion used as EOF controller. The suitability of the BGE composition for reliable and sensitive analyses was assessed as high absorbances of the analytes, low detector noise, good resolution between the analytes and high theoretical plate numbers. The final compositions of the electrolyte solutions were the following: 4 m*M* PZDA and 0.5 m*M* MTAH (pH 10.6), 4 m*M* PDA and 0.5 m*M* MTAB (pH 11.0) or 7 m*M* QUIN and 0.5 m*M* MTAB (pH 10.2). The detection in PZDA background electrolyte solution was performed at 280 nm and that in the PDA and QUIN solutions at 266 nm. The final parameters are presented in Table 1.

The electrophoretic mobilities of the DCAs are strongly dependent on the pH of the BGE solution. Since the pK_a values of the dicarboxylic acids that were studied lie between 1 and 6.7, values of pH above 9.00 were selected to ensure full ionisation of the DCAs. The pK_a values of the analytes are shown in Table 2 [20,21].

The BGE solutions prepared of PDZA or PDA

Table 2
pK_a values of the dicarboxylic acids

	Literature [20]		Estimation according to Pallas [21]	
	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}
Oxalic acid	1.27	4.27	0.99	6.68
Malonic acid	2.85	5.70	2.77	5.38
Succinic acid	4.21	5.64	3.79	4.93
Glutaric acid	4.32	5.42	4.22	5.05
Adipic acid	4.41	5.41	4.37	5.06
Pimelic acid	–	–	4.42	5.06
Suberic acid	–	–	4.61	5.22
Azelaic acid	–	–	4.61	5.22
Sebacic acid	–	–	4.61	5.22

Table 1
Experimental conditions for CE analysis

Condition	PZDA[a]	PDA[b]	QUIN[c]
Electrolyte	4.0 m*M* PZDA	4,0 m*M* PDA	7.0 m*M* QUIN
solution	0.5 m*M* MTAH[d]	0.5 m*M* MTAB[e]	0.5 m*M* MTAB
	pH 10.6	pH 11.0	pH 10.2
Polarity	Negative	Negative	Negative
Detection	Indirect 280 nm	Indirect 266 nm	Indirect 266 nm
Voltage	21 kV	24 kV	20 kV
Injection	50 mbar, 6 s	50 mbar, 6 s	50 mbar, 5 s

[a] 2,6-Pyrazinedicarboxylic acid.
[b] 2,6-Pyridinedicarboxylic acid.
[c] 2,3-Pyridinedicarboxylic acid.
[d] Myristyltrimethylammonium hydroxide.
[e] Myristyltrimethylammonium bromide.

reagent and MTA were found to give the largest absorption difference between the dicarboxylic acids and the UV-absorbing electrolyte reagent at the detection wavelengths 280 and 266 nm. QUIN was not as good a chromophore as the 2,3-substituted pyrazine or 2,6-substituted pyridine dicarboxylic acids (Fig. 1). The electrophoretic mobilities of the analytes were fastest in the PZDA solution. The dicarboxylic acids migrated according to their molar masses, i.e., more slowly from oxalic acid to sebacic acid. The analytes with shortest hydrocarbon chains had electrophoretic mobilities equal to those of PDZA, PDA and QUIN anions and the peaks for the analytes were high and narrow. In view of the better resolution and sensitivities, only PZDA and PDA solutions containing MTA were used in further studies.

Our results agree with those of Li et al. [22], that the composition of the BGE solution should be carefully chosen to obtain a match between the mobilities of the analytes and the mobility of the buffering ion. The apparent velocity (u) is the combination of its electrophoretic velocity and its movement in response to EOF:

$$u = u_{ep} + u_{eo} = \mu_a E = (\mu_{ep} + \mu_{eo})E \quad (1)$$

The electrophoretic mobility, μ_a, is determined from the migration time (t_m), the field strength ($E = V/L_{tot}$) in a capillary of total length L_{tot}, and the migration window L_{det} by the following equation:

$$\mu_a = (L_{det}/t_m)(L_{tot}/V) \quad (2)$$

Electroosmotic mobility (μ_{eo}) was determined experimentally by injecting methanol and measuring t_{eo} when it appears at the detection point:

$$\mu_{eo} = (L_{det}/t_{eo})(L_{tot}/V) \quad (3)$$

where V is the applied potential, t_m is the migration time of the analyte and t_{eo} is the migration time of the electroosmotic flow. Combining Eqs. (1)–(3) gives:

$$\mu_{ep} = L_{det}\, L_{tot}/Vt_m - L_{det}L_{tot}/Vt_{eo} \quad (4)$$

There were only minor differences in the electrophoretic migrations of the DCAs and in their resolution, when PZDA and PDA BGE solutions were used at pH 10.6 and 11.0, respectively (Table 3). The electrophoretic mobilities ranged between 3.0×10^{-4} and 7.0×10^{-4} cm^2 V^{-1} s^{-1}, which is the same magnitude as reported by Soga and Ross [15,23].

The concentrations of the electrolytes were kept as low as possible to prevent Joule heating, which increases the baseline noise. Concentrations were investigated in the range 1 to 20 m*M*. Higher concentrations were found to decrease the peak sensitivity and reduce the repeatability of the analyses. For example, detection sensitivity was 35–50% better with 4 m*M* PDA electrolyte solution than with 20 m*M* PDA electrolyte solution. The optimal electrolyte concentrations were 4, 4 and 7 m*M* for PZDA, PDA and QUIN, respectively

Concentrations between 0.1 and 2.0 m*M* were tested for the two EOF modifiers, MTAH and MTAB. The co-ion in the modifier did not play any role at such low concentrations. However, to avoid ion-pair formation between BGE and the amine modifier, the lowest possible concentration of ammonium salt was added to the BGE; this was 0.5 m*M* for both MTAB and MTAH. This concentration was high enough to reverse the EOF totally and all analytes had migration times of less than 5 min, increasing with the number of carbons in the chain.

3.2. Validation of the electrophoretic procedure

3.2.1. Repeatabilities

Repeatabilities of the different methods were determined with a mixture of DCAs at concentration of 10 mg/l each. RSDs for the migration times, peak heights and peak areas were calculated from the absolute values of within-day runs ($n=6$) and day-to-day runs (3 days, six repetitions). The results are compiled in Table 4. The experiments in the PZDA electrolyte solution gave RSDs below 0.5% for the migration times of all DCAs except suberic acid, and RSDs of 1–15% for peak heights and areas for all DCAs except succinic and glutaric acids, which were overlapped with the system peak. With PDA electrolyte solution, RSDs for the migration times of the DCAs were below 1% for within-day and between 2 and 4% for day-to-day experiments. RSDs for peak heights and areas were lower than 10%. With a few exceptions, as can be seen, precisions were better for migration times measured in PZDA solution. However, precisions were better for peak areas and

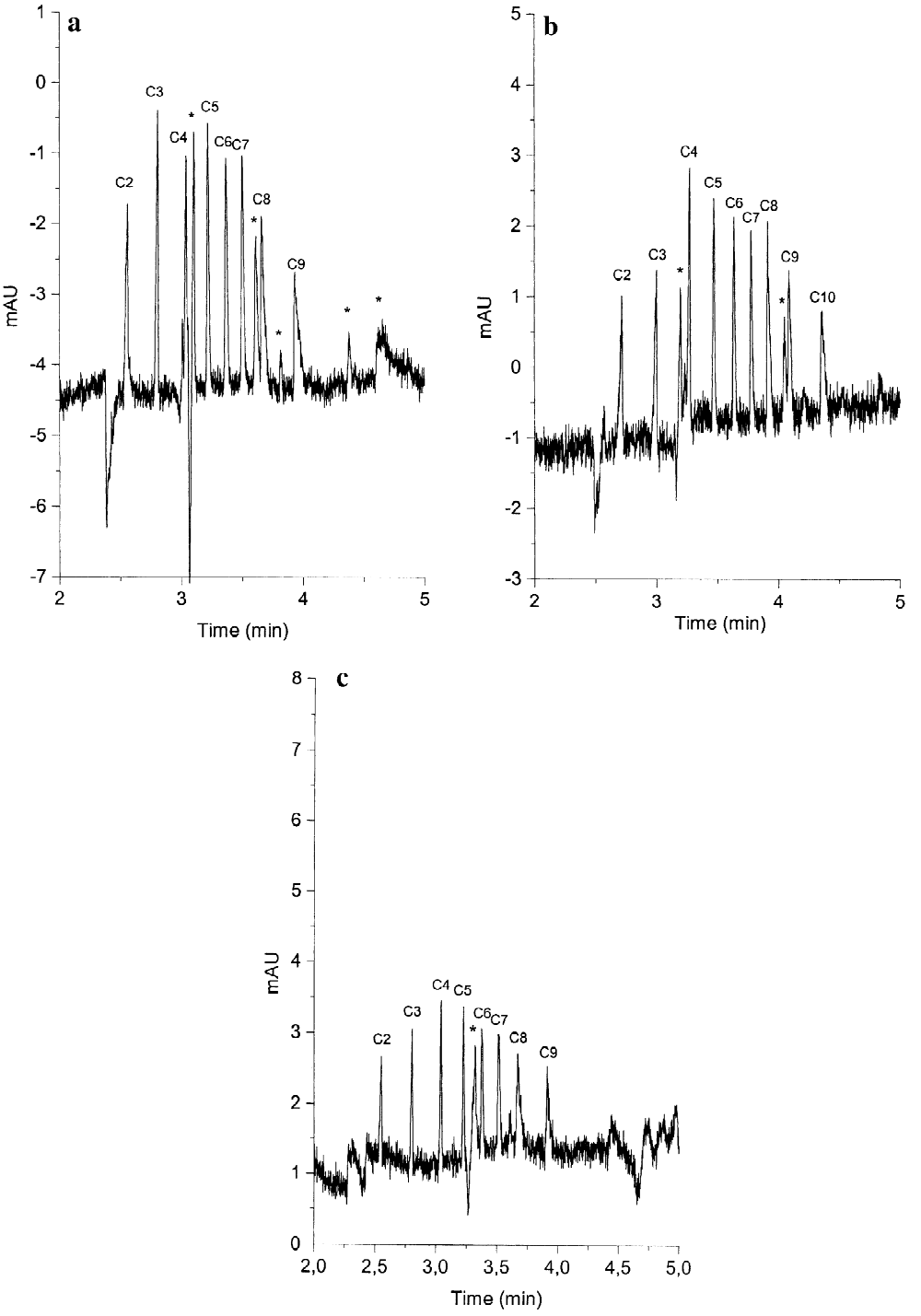

Fig. 1. Separation of nine DCAs in 10 mg/l mixture in (a) 4 m*M* PZDA, 0.5 m*M* MTAH (pH 10.6), (b) 4 m*M* PDA, 0.5 m*M* MTAB (pH 11.0) and (c) 7 m*M* QUIN, 0.5 m*M* MTAB (pH 10.2). Peaks: C2, oxalic acid; C3, malonic acid; C4, succinic acid; C5, glutaric acid; C6, adipic acid; C7, pimelic acid; C8, suberic acid; C9, azelaic acid; C10, sebacic acid; and *unidentified peak.

Table 3
Electrophoretic mobilities of the analytes: total length, 58.5 cm; length to the detector, 50 cm; V=21/24 kV (PZDA/PDA) (n=6)

	PZDA		PDA	
	t_m (min)	μ(ion) ($\times 10^{-4}$ cm^2 V^{-1} s^{-1})	t_m (min)	μ(ion) ($\times 10^{-4}$ cm^2 V^{-1} s^{-1})
Oxalic acid	2.156	7.047	2.189	6.351
Malonic acid	2.358	6.127	2.403	5.523
Succinic acid	2.576	5.292	2.613	4.846
Glutaric acid	2.733	4.775	2.765	4.417
Adipic acid	2.859	4.400	2.815	4.104
Pimelic acid	2.972	4.092	2.994	3.856
Suberic acid	3.068	3.847	3.092	3.640
Azelaic acid	3.201	3.532	3.210	3.400
Sebacic acid	3.399	3.111	3.403	3.041
EOF	6.483	3.719	6.936	2.929

t_m, migration time.

heights measured in PDA solution. For PDA, the within-day variations of the migration times were noticeably smaller than those over 3 days, surprisingly this was not the case with PZDA solution. The high precision of the optimized methods allowed them to be applied to the analysis of dicarboxylic acids in aerosol particle samples.

3.2.2. Detection limits and linearity

The detection limits (LOD) of DCAs were studied with PZDA and PDA electrolyte solutions. The results are presented in Table 5. In PZDA solution, LODs ranged from 1.0 mg/l for malonic acid to 9.1 mg/l for azelaic acid, with a signal-to-noise ratio of 3, while in PDA solution the values ranged from 1.1 mg/l for suberic acid to 7.6 mg/l for sebacic acid.

Linear correlations of peak height against concentration of the analyte are also listed in Table 5. The analytes had linear correlations in the range 0.5–100 mg/l. Oxalic and malonic acids had the widest linear ranges in PZDA solution from 1 to 100 mg/l, and succinic and glutaric acids had widest linear ranges in PDA solution from 3 to 100 mg/l. Overall, linearity ranges were wider in PDA solution than in PZDA solution because at higher concentrations succinic, glutaric, adipic, pimelic and suberic acids were overlapped in PZDA.

Table 4
Precisions of the absolute values of within- and day-to-day determinations of DCAs in PZDA and PDA solutions

	RSD (%)					
	Within-day (n=6)			Day-to-day (n=18)		
	t_m	Area	Height	t_m	Area	Height
PZDA						
Oxalic acid	0.32	7.47	3.89	0.34	6.89	3.61
Malonic acid	0.31	4.10	4.02	0.36	2.26	1.32
Succinic acid	0.34	21.9	21.4	0.35	19.4	18.6
Glutaric acid	0.42	25.7	20.2	0.39	13.9	10.1
Adipic acid	0.48	8.80	11.3	0.42	6.90	8.30
Pimelic acid	0.44	5.67	14.6	0.41	5.63	6.45
Suberic acid	0.71	10.6	8.05	0.31	15.5	12.1
Azelaic acid	0.49	15.2	6.97	0.09	3.93	3.00
Sebacic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PDA						
Oxalic acid	0.18	2.28	3.96	2.44	1.52	5.87
Malonic acid	0.26	6.92	8.70	2.87	10.5	6.55
Succinic acid	0.34	17.1	6.73	3.32	13.8	22.9
Glutaric acid	0.49	9.59	12.0	3.48	4.20	6.74
Adipic acid	0.60	6.93	7.76	3.71	9.35	8.04
Pimelic acid	0.69	7.52	11.6	3.91	9.20	4.41
Suberic acid	0.76	4.55	7.65	4.07	2.10	10.7
Azelaic acid	0.81	14.7	7.08	4.08	11.8	6.31
Sebacic acid	0.94	2.80	3.25	3.90	4.28	3.73

Table 5
Linearities, LODs, correlation coefficients and linear calibration equations for determinations of DCAs in PZDA and PDA solutions: $Y = ax + b$ ($n = 6$) (n.d. = not detected)

	Linearity range (mg/l)	LOD (mg/l)	R^2	a	b
PZDA					
Oxalic acid	3–100	3.104	0.945	0.096	2.070
Malonic acid	1–100	0.930	0.963	0.163	2.939
Succinic acid	3–20	1.533	0.986	0.125	2.610
Glutaric acid	3–20	2.632	0.984	0.369	0.610
Adipic acid	3–20	2.660	0.953	0.348	0.319
Pimelic acid	3–20	1.624	0.961	0.187	1.299
Suberic acid	5–20	4.858	0.991	0.226	0.544
Azelaic acid	10–50	9.131	0.990	0.062	0.780
Sebacic acid	n.d.	n.d.	n.d.	n.d.	n.d.
PDA					
Oxalic acid	3–50	3.033	0.967	0.0895	0.947
Malonic acid	5–50	3.431	0.958	0.0668	1.434
Succinic acid	3–100	1.957	0.998	0.205	0.843
Glutaric acid	3–100	2.347	0.997	0.234	1.073
Adipic acid	3–50	3.020	0.991	0.254	0.453
Pimelic acid	3–50	3.220	0.989	0.195	0.654
Suberic acid	3–50	1.117	0.993	0.147	1.782
Azelaic acid	3–50	2.832	0.983	0.126	0.678
Sebacic acid	10–50	7.621	0.994	0.081	0.573

3.3. Aerosol particle samples

Malonic, succinic, adipic and suberic acids were detected in the water-soluble fraction of the aerosol particle samples. DCAs were identified through reference to standards spiked in the samples. The electropherogram of an aerosol sample is shown in Fig. 2. The most intensive peak was assumed to be the inorganic fraction of the sample overlapping with oxalic acid, because oxalic acid is normally the most abundant DCA in aerosol particles [5,10]. The found DCA concentrations were estimated to be tens to hundreds of ng/m^3 in the detected aerosol samples.

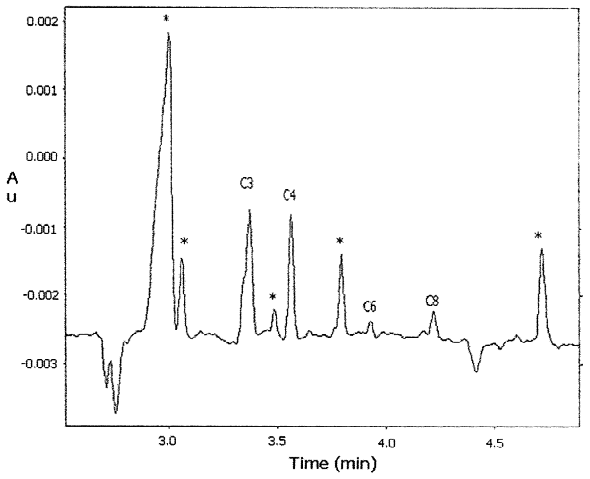

Fig. 2. Electropherogram of an aerosol particle sample. Analysis was made with 4 m*M* PDA and 0.5 m*M* MTAB solution (pH 11.0). Peaks: *unidentified peaks; C3, malonic acid; C4, succinic acid; C6, adipic acid; and C8, suberic acid.

4. Conclusions

Simple and repeatable methods were developed for the analysis of dicarboxylic acids in aerosol particles. RSDs for migration times were below 0.5% in PZDA solution and below 1% for within-day and between 2 and 4% for day-to-day runs in PDA solution. Peak heights and areas mostly deviated between 1 and 15% in PZDA solution, while in PDA solution RSDs were less than 10% with only a few exceptions. Detection limits from 1.0 to 9.1 mg/l for DCAs in PZDA electrolyte solution and detection

limits from 1.1 to 7.6 mg/l were obtained for PDA solution.

Capillary electrophoresis is efficient, fast and convenient for the determination of DCAs in aerosol particles. The methods developed and optimised in this study were both fast and repeatable. The technique was relatively sensitive for indirect UV detection of the DCAs. The methods were applied to aerosol samples and the presence of malonic, succinic, adipic and suberic acids was demonstrated.

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