

Introduction

Organic compounds are a main fraction of atmospheric aerosol particles. They play an important role in atmospheric chemistry, biogeochemical cycles, and with regards to climatic and health effects. Because of their low vapor pressure dicarboxylic acids (DCA) like oxalic acid, malonic acid, succinic acid and even the higher homologues as well as some of their hydroxylated homologous compounds are frequently found in the tropospheric particle phase (Saxena and Hildemann 1996). They at least partly result from a variety of chemical conversion reactions in either the gas or condensed phase environment (Kawamura and Sakaguchi 1999). In this approach capillary electrophoresis (CE) has been used to determine selected organic acids of size resolved atmospheric aerosol particles. Samples were taken in October/November 2001 during FEBUKO (*field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes*) field campaign in a forestal region in Germany (Thüringer Wald).

Sampling and sample preparation

For sampling a five-stage low-pressure cascade impactor (Bernier-type with 50% cutoffs: 0.05, 0.14, 0.42, 1.2, 3.5, and 10 μm) equipped with precleaned Tedlar® foils as impaction substrates was used. After sampling the foils were cut into small pieces and the water soluble particle content was extracted with 2 ml deionized water by shaking, sonicating, and shaking again for 10 min each.

CE Parameters

For CE-analysis a Spectra Phoresis 1000 instrument from Thermo Separation Products (now Thermoquest) was used. Main parameters of separation are shown in Table 1.

Table 1: Parameters of CE separation

capillary length	70 cm
capillary length to detector	63 cm
capillary inner diameter	75 μm
applied temperature	25 °C
applied voltage	- 29,4 kV
composition of electrolyte	10 mmol/l p-aminobenzoic acid 8 mmol/l diethylenetriamine 3,5 mmol/l NaOH (pH=9,6)
injection mode	hydrodynamic : 10,3 kPa for 30 s
detection mode	indirect at 254 nm

Electropherograms

With the described conditions it was possible to separate successfully the anions of 16 DCA and 8 other ions in a single run.

In Figure 1 an electropherogram of a 4 $\mu\text{mol/l}$ standard solution is given.

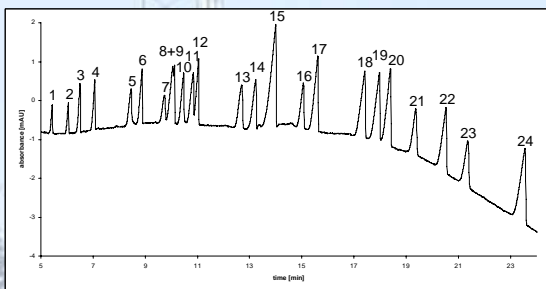


Figure 1: Electropherogram of standard solution (4 $\mu\text{mol/l}$ each)

Many of these compounds were identified in the aerosol samples. Figure 2 shows an electropherogram of a real sample.

Peak identification for figures 1 and 2:

- 1 chloride, 2 nitrate, 3 sulfate, 4 oxalate,
- 5 tartrate, 6 malonate, 7 formate,
- 8 fumarate, 9 maleinate, 10 tartrate,
- 11 malate, 12 succinate, 13 citramalate,
- 14 glutarate, 15 hydrogen carbonate,
- 16 methanesulfonate, 17 adipate,
- 18 2,2-dimethyl glutarate, 19 pimelate,
- 20 3,3-dimethyl glutarate,
- 21 trifluoroacetate, 22 suberate,
- 23 acetate, 24 azelate

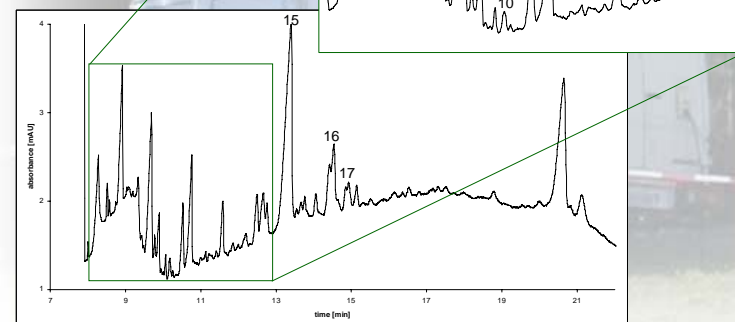


Figure 2: Electropherogram of aerosol particulate matter extract

Repeatability and reproducibility

To determine short- and long-term precision of the corrected peak area (peak area/migration time, CPA), a mixture of dicarboxylic acids at the concentration of 4 $\mu\text{mol/l}$ was measured ten times on a single day and on different days over 3 months. The relative standard deviations (RSD) of mean CPAs are shown in Table 2.

Table 2: Precision of CPA

	intra-day RSD [%]	inter-day RSD [%]
oxalate	1,4	2,1
tartrate	1,3	6,7
malonate	1,0	2,2
fumarate	1,1	2,4
maleinate	1,1	2,4
tartrate	1,2	4,9
malate	1,8	2,5
succinate	2,8	1,7
citramalate	2,2	3,1
glutarate	3,2	6,3
adipate	1,8	7,0
2,2-Dimethyl glutarate	2,1	5,7
pimelate	1,8	5,4
3,3-Dimethyl glutarate	2,1	5,2
suberate	2,4	4,2
azelate	2,2	4,2

Detection limits

Limits of detection (LOD) for those compounds found in the real sample were evaluated from calibration graph following DIN 32645. The results are shown in Table 3. The absolute detection limit was calculated using the volume of sample solution filled into the capillary during 30 s injection (0,32 μl).

Table 3: Detection limits

	LOD [$\mu\text{mol/l}$]	LOD [$\mu\text{g/l}$]	absolute LOD [$\mu\text{g/l}$]
oxalate	0,04	3,1	1,0
tartrate	0,03	3,2	1,0
malonate	0,03	3,3	1,1
formate	0,05	2,1	0,7
fumarate	0,04	4,0	1,3
maleinate	0,04	4,0	1,3
tartrate	0,04	6,4	2,0
malate	0,01	1,8	0,6
succinate	0,01	1,0	0,3
citramalate	0,09	12,8	4,1
glutarate	0,15	19,7	6,3
methanesulfonate	0,06	5,8	1,9
adipate	0,04	6,4	2,0
acetate	0,09	5,2	1,7

Results

In Figure 3 particulate DCA-concentrations for one sampling period are shown. Concentrations for each acid are summed up over all five impactor stages (particle diameter 0,056 – 10 μm). Oxalic acid was the most abundant, followed by malonic, succinic and glutaric acid (incl. non resolved isomers methyl succinic acid and dimethyl malonic acid). Hydroxylated and unsaturated acids showed smaller concentrations. Highest concentrations of the acids were found in particle diameter range 0,42 – 1,2 μm (stage 3) where also total particle mass was highest (not shown).

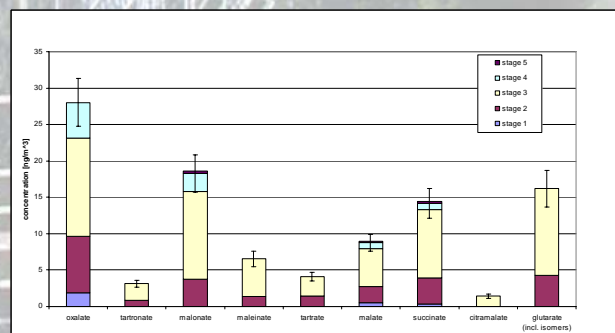


Figure 3: DCA concentrations for sampling period 26-27/10/02

Acknowledgment

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References

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