

Determination of organic acids in tropospheric aerosol particles by capillary electrophoresis

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Organic compounds are a main fraction of the atmospheric aerosol besides inorganic salts and black carbon. 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 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. They at least partly result from a variety of chemical conversion reactions in either the gas or condensed phase environment.

In this approach capillary electrophoresis (CE) has been used to determine selected organic acids of size segregated atmospheric aerosol particles.

Samples were taken during FEBUKO field campaign in a forestal region in Germany (Thüringer Wald).

CE has some important advantages for the analysis of ions in aerosol particles compared to the commonly used ion chromatography (IC) or gas chromatography (GC). It is a simple and fast technique, which needs no sample purification or preparation. The absolute detection limits are very low (below 1 pMol) and it has a large range of signal-to-concentration linearity (up to 4 orders of magnitudes for this approach) [Neusüß, 2000]. Thus difficult matrices with strongly changing concentrations and compositions such as aerosol samples may be investigated. The separation efficiency is usually much higher than in liquid chromatography and the required sample amount is low (down to <1 µL).

For sampling a five-stage low-pressure cascade impactor (Berner-type with 50% cutoffs: 0.05, 0.14, 0.42, 1.2, 3.5, and 10 µm) was used. A humidity-controlled tube bundle served as the inlet device. Tedlar foil was used to determine ionic compounds.

A Spectra Phoresis 1000 instrument from Thermo Separation Products (now Thermoquest) equipped with a fused silica capillary with an inner diameter of 75 µm and a total length of 70 cm (63 cm to the detector) was used. The applied electrical field is 420 V cm⁻¹. Hydrodynamic injection is applied. A pressure difference of 10.3 kPa for 30 s is used for the determination of the organic anions.

The buffer to separate the anions consists of an aqueous solution of p-aminobenzoate (10 mmol L⁻¹), NaOH (resulting in a pH of 9.6), and 8 mmol L⁻¹ diethylenetriamine. Indirect detection is performed with a UV detector working at 254 nm.

Identification of organic acids is performed by adding standards to the sample. Because of high separation efficiency of capillary electrophoresis, this method leads to a high certainty of identification. The peak area is used for quantification.

With described conditions it was possible to separate successfully the anions of 12 dicarboxylic acids, 4 hydroxylated dicarboxylic acids, as well as formiate, acetate, trifluoroacetate, and methanesulfonate (MSA) in a single run. Many of these compounds were identified and quantified in the environmental samples.

References:

Neusüß, C., Pelzing, M., Plewka, A. and Herrmann, H., 2000, A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results, *J. Geophys. Res.*, **105**, D4, 4513