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Quantification of organic acids in particulate matter by coupling of thermally assisted hydrolysis and methylation with thermodesorption-gas chromatography–mass spectrometry

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ABSTRACT

A quantitative method for the determination of organic acids in atmospheric particles is developed. The method couples a derivatisation step (thermally assisted hydrolysis and methylation) and a Curie point pyrolyser as a thermal desorption technique and gas chromatography–mass spectrometry (CPP-GC–MS). Among the reagents tested (tetramethylammonium hydroxide (TMAH), tetramethylammonium acetate (TMAAc) and phenyltrimethylammonium hydroxide (TMPAH)), the best performance was found using TMAAc as a derivatisation reagent for the reaction time of 4 s at 510 °C as heating temperature. Calibration was performed for a series of fatty acids (FA), dicarboxylic acids (DCA) and terpenoic acids (TA) under these conditions. Coefficients of determination (R^2) were between 0.94 and 0.98. Limits of detection (LOD) were in the nanogram-range between 0.1 and 3.6 ng. The method is applied on atmospheric particle samples to obtain the quantification reproducibility and quantification limits. Reproducibility was determined in terms of relative standard deviations (RSD) for ambient aerosol samples collected by a high-volume-sampler (HVS, RSD = 6–45%, $n = 10$) and a Berner impactor (BI, RSD = 5–34%, $n = 10$). Based on 24 h sampling time the developed method enables quantification of all three classes of acids for both sampling techniques. Calibration data and presented volume concentrations are compared with literature data. A comparison with an off-line methylation-GC–MS using BF_3 as a derivatisation reagent and capillary electrophoresis coupled mass spectrometry (CE-MS) showed a good agreement. Minimal sample preparation is the main advantage of the developed method. Depending on the sensitivity requirements the present method can be a fast and simple alternative to GC–MS techniques with conventional sample preparation steps for semi-volatile organic acids.

1. Introduction

Atmospheric particles play an important role in atmospheric chemistry, climate processes and human health. Organic carbon constitutes a significant fraction of atmospheric fine particles [1]. The concentrations and constituents of organic fraction of the atmospheric particles are highly variable and only a small fraction of the organic compounds can be identified positively using authentic standard compounds. The compounds, which are typically found in atmospheric particles, include alkanes, alkenes, polycyclic aromatic hydrocarbons (PAH), sterols, alcohols, carbonyl compounds, carboxylic acids and their keto derivatives, amines and amino acids, aromatics, carbohydrates and humic-like substances (HULIS) (e.g. [2–10]). Among those the most important components identified in terms of their mass fractions are polar substances such as aliphatic dicarboxylic acids, alkanoic acids and aromatic polycarboxylic acids (e.g. [4,10–13]).

The chemical characterisation of atmospheric particles is important for a fundamental understanding of atmospheric processes. This requires effective collection of the particles and highly sensitive and specific analytical methods, due to low sample amounts, especially for size segregated samples and the extremely complex nature of sample matrix.

Until now most of published derivatisation GC–MS methods for polar organic compound analysis are based on solvent extraction, clean up and off-line derivatisation steps followed by GC–MS analysis [4,12,14–18]. Clearly, time-consuming sample preparation steps and dilution of samples are the disadvantages of these methods. Direct thermal desorption techniques are alternative sample preparation and injection methods for GC–MS [13,19–27]. A Curie point pyrolyzer (CPP) is demonstrated to be a good alternative to a conventional thermal desorption instrument due to its high accuracy, low sample requirement (a few μg), speed and simplicity [13,25,26]. The technique was used primarily earlier for thermal

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decomposition and characterisation of polymers. It was found that thermally stable compounds do not decompose, but merely evaporate during the CPP process [28,29]. The CPP-technique can be applied for the analysis of polycyclic aromatic and aliphatic hydrocarbons, poly-chlorinated biphenyls, organic halogens and hetero-aromatics in soils [28,29], as well as hydrocarbons in shale oil [30]. These studies have found comparable results to classical solvent extraction methods. Neusüß et al. [13] successfully applied the CPP for the analysis of organic compounds in size segregated atmospheric aerosol samples; however, the application was limited to non-polar organic compounds due to the adsorptive properties of polar organic compounds.

The coupling of on-line derivatisation with thermodesorption-GC–MS performed in this study is based on the method published by Robb and Westbrook [31] for the analysis of fatty acids using tetramethylammonium hydroxide (TMAH) as a derivatisation reagent. The derivatisation is performed on the methylation of acid protons in organic compounds by strong basic quaternary *N*-methylammonium hydroxide and is extensively described elsewhere [32]. The combination of the TMAH derivatisation reagent and the pyrolysis technique is successfully demonstrated by Challinor [33] for the analysis of polyester by saponification and methylation of a mixture of fine polymer particles and an aqueous 25% w/w TMAH solution. The so-called thermally assisted hydrolysis and methylation (THM) was applied for a variety of lipids [34–37] and offers simple sample preparation, minimal sample amount, high yields and acceptable reproducibility [35–37]. Coupling of THM with pyrolyser based thermodesorption-GC–MS for the analysis of polar substances in atmospheric particles was first published by Gelencsér et al. [38] and Subbalakshmi et al. [39]. Both groups investigated the nature of so-called humic-like substances (HULIS) using this technique.

Fatty acids, dicarboxylic acids, hydroxybenzoic acids and several polysaccharides were identified by these and other groups [40,41]. In these studies, pyrolysis and thermodesorption processes were not clearly differentiated because both processes can proceed under the temperature ranges used in these studies (400 °C [40,41] to 700 °C [41]). Furthermore, results were only discussed qualitatively in these studies and quantification was hindered due to low reproducibility [41].

The primary aim of the present study is to optimise the combination of THM with CPP-GC–MS for the qualitative and quantitative determination of polar organic compounds in atmospheric particles, especially fatty acids (FA), α,ω-dicarboxylic acids (DCA) and carboxylic acids originating from monoterpene oxidation (terpenoic acids, TA). The successful application of this combination for the analysis of polar organic compounds in size segregated atmospheric particle samples is demonstrated.

2. Experimental

2.1. Reagents and material

Aqueous solutions of tetramethylammonium hydroxide (TMAH, 25%), tetramethylammonium acetate (TMAAc, 50%), phenyltrimethylammonium hydroxide (TMPAH, 25%) and a 1.3 mol L^{-1} methanolic solution of BF_3 used as derivatisation reagents were purchased from Fluka (St. Louis, MO, USA). Tetracosane-*d*50 from Chiron (Trondheim, Norway) was used as internal standard. The following standards were used: C_{10}–C_{22} fatty acids (FA) from Promochem (Wesel, Germany), C_6–C_{10} α,ω-dicarboxylic acids (DCA), pinic acid and pinonic acid (TA) from Sigma–Aldrich (St. Louis, MO, USA). Norpinonic acid was synthesised by oxidative cleavage of verbenone in two-phase procedure as described by Cella [42]. Stock solutions of 1 mg mL^{-1} standard compounds in *n*-hexane were prepared and further diluted with suitable solvents.

Pyrolysis foil (1 × 2 cm) is an iron (45%)–nickel (55%) alloy, which leads to a heating temperature of 510 °C (ThyssenKrupp VDM, Werdohl, Germany).

2.2. Samples

Sampling of atmospheric particles by Berner impactors was performed on aluminium foils (37 mm, 0.45 μm, Schleicher & Schuell TE36, Dassel, Germany). Impactor stages with aerodynamic cut-off diameters of 0.05–0.14 μm (stage 1), 0.14–0.42 μm (stage 2), 0.42–1.2 μm (stage 3), 1.2–3.5 μm (stage 4) and 3.5–10 μm (stage 5) were used. Quartz fibre filters (MK 360, Munktell, Sweden) were used for sampling by high-volume-sampler (HVS, Digitel Elektronik AG, Hegnau, Switzerland). The HVS samples with an upper aerodynamic diameter of 10 μm (PM_{10}) were analysed. The filters were pre-treated in an oven for 24 h at 105 °C to reduce the blank content of carbonaceous material. Although the conditioning temperature was relatively low for the quartz fibre filters, this temperature was chosen as lower organic carbon blank values were found at this temperature than higher temperatures.

Samples were taken at two sites in summer time: (1) rural background samples at the IfT research station near the small village of Melpitz located approximately 41 km northwest of Leipzig, Germany and (2) suburban samples at the IfT campus site in a residential area in the north-east of Leipzig (Table 1). Sampling duration was 24 h for both the HVS and Berner impactors. The sample flow rates of the HVS and Berner impactors were 500 and 75 L min^{-1}, respectively.

Samples for the method comparison of monoterpene oxidation acids (TA) were generated in IfT aerosol-chamber. A detailed description of α-pinene ozonolysis and sample collection is given elsewhere [43].

2.3. Sample preparation

For the solvent extraction of the HVS samples, a half quartz fibre filter piece (769.7 mm^2) was treated 20 h by Soxhlet extraction with a methylene chloride: methanol (4:1, v/v) mixture. 5 mL of isooctane was added and the extract volume was reduced to approximately 1 mL by rotary evaporation, transferred into a conical vial and further reduced to dryness under a gentle nitrogen stream. BF_3 (300 μL, ~1.3 mol L^{-1} in methanol) was added and kept at 60 °C for 10 min. After cooling the solution was extracted four times with 250 μL *n*-hexane and the combined extracts were dried under a gentle nitrogen stream. Residues were re-diluted in *n*-hexane and directly injected for GC–MS analysis.

Table 1
Sampling data.

Device	Site location	Site description	Date	Application
Digitel PM_{10}	Melpitz	Rural	13 July 2005	Method comparison
Digitel PM_{10}	Melpitz	Rural	29 July 2005	Reproducibility, size segregated measurements
Berner	Melpitz	Rural	10 July 2005	Size segregated measurements
Berner	IfT	Suburban	13 July 2005	Reproducibility, size segregated measurements