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Particle-into-liquid sampler on-line coupled with solid-phase extraction-liquid chromatography–mass spectrometry for the determination of organic acids in atmospheric aerosols

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ABSTRACT

In the present study, sample collection and preparation were directly integrated with a chromatographic system by coupling a particle-into-liquid sampler for the first time on-line with solid-phase extraction-liquid chromatography–tandem mass spectrometry. Several organic acids, such as adipic, hydroxyglutaric, mandelic, vanillic, *cis*-pinonic, pinic, azelaic and sebacic, were used in the research. For sample pretreatment and concentration, strong anion exchange material was used in the extraction. Sampling, extraction and analysis conditions were optimized to obtain reliable information about aerosol chemical composition. To evaluate the performance of the on-line coupled system, half of each sample was analysed on-line and the other half was derivatized and analysed off-line by gas chromatography–mass spectrometry. Comparison of the two techniques with use of *t*-test showed the results to be in an excellent agreement. Limits of detection of studied acids in on-line system were between 0.1 and 0.9 ng. The on-line coupled system is fast and reliable and a promising tool for the real time analysis of organic acids in atmospheric aerosols.

1. Introduction

The Earth's climate is a highly dynamic and complex system in which aerosols have been increasingly recognized to play a key role (Intergovermental Panel on Climate Change, IPCC). Aerosols may affect the climate through complex processes, directly by absorbing and reflecting radiation, and indirectly by changing the properties of clouds. Because of the complexity, quantification of the climate effects of aerosols is still highly uncertain and is a challenging aspect in climate research [1]. Better understanding of the effects of aerosols requires more information on aerosol chemistry. It is known that a large fraction (>50%) of the submicron aerosol mass in the troposphere consists of organic material [2], especially oxygenated compounds. Highly oxidized compounds, such as carboxylic acids and keto- and dicarboxylic acids, are of greatest interest because of their low saturation pressure and consequent high aerosol forming potential.

For the determination of aerosol chemical composition, particles are usually collected onto filters, and after the extraction, the compounds of interest are analysed by gas or liquid chromatography with mass spectrometric detectors [3–5]. Recently, direct mass spectrometric techniques have been used for the determination of aerosol chemical composition [6–8]. Unfortunately all these techniques suffer from many disadvantages, including long sampling time, oxidation, gas-phase adsorption, and mixed mass spectra. As well, off-line sample treatment and analysis may introduce undesirable uncertainties.

In our previous work, a particle-into-liquid sampler (PILS) was applied to the collection of aerosol particles (PM 2.5), and samples were analysed by gas chromatography–mass spectrometry after liquid–liquid extraction [9] or by liquid chromatography–mass spectrometry after extraction with mixed phase anion exchange material [10]. The results demonstrated that PILS can be successfully used as a particle collection device not only for the determination of inorganic and small organic ions but also for the determination of less abundant species, such as the oxidation products of α-pinene. However, the off-line treatment needed for PILS samples and the subsequent analysis were laborious and time consuming.

A recent trend in the development of analytical methodologies is integration of the different analytical steps. In integrated on-line systems, extraction, clean-up, separation and detection

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steps are typically connected with each other and the whole analytical procedure takes place in a closed, usually automated system. Several of the problems associated with the traditional approaches are then avoided. Additional benefits are the increased sensitivity and reliability because the sample clean-up tends to be more effective [11]. The most common on-line systems are solid-phase extraction-liquid chromatography–mass spectrometry, and automated commercial systems are available. In this work, PILS aerosol sampling technique was on-line coupled with solid-phase extraction-liquid chromatography–tandem mass spectrometry. The extraction step was first optimized with a standard mixture of several biogenic organic acids to accept the liquid PILS sample flow. Then the compatibility of the extraction and liquid chromatographic steps was adjusted. Finally, the on-line system was applied to the analysis of organic acids in aerosol samples and the results were compared with those obtained by GC–MS after off-line extraction and derivatization.

2. Experimental

2.1. Chemicals

Azelaic acid (>99%), maleic acid (99%), tartaric acid (99.5%), malic acid (99.5%), malonic acid (98%), vanillic acid (97%) and sebacic acid (purum) were purchased from Fluka Chemie GmbH (Buchs, Switzerland). Adipic acid (99%) and mandelic acid (99.5%) were from BDH Chemicals Ltd (Poole, England). Benzoic acid (pro-analysis) was obtained from Schering-Kahlbaum (Berlin, Germany). Pinic acid (library of rare chemicals, no purity available), *cis*-pinonic acid (98%), caprylic acid (99%) and sinapic acid (99%, internal standard) were obtained from Sigma–Aldrich Chemie GmbH (Steinheim, Germany). Methanol and pyridine were purchased from J.T. Baker (Deventer, The Netherlands), while dichloromethane was from LabScan (99.8%, Dublin, Ireland). For the HPLC analysis, acetonitrile (HPLC Far UV, Lab Scan, Analytical Sciences, Poland) and water (DirectQ-UV, Millipore Corp., Billerica, USA) with acetic acid (99%, Fluka Chemie GmbH, Buchs, Switzerland) were used.

A solution of N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), purchased from Sigma–Aldrich, was used as silylation reagent for the derivatization.

3-Hydroxyglutaric acid was synthesised in the laboratory as described elsewhere [12]. However, a purification step involving solid-phase extraction with anion exchange material was added and the purity was confirmed as described in Ruiz-Jimenez et al. [13].

For the denuder coating, potassium iodide was purchased from Merck (Darmstadt, Germany), glycerol from Sigma–Aldrich (Steinheim, Germany) and XAD-2 resin (polystyrene-divinylbenzene) from EGA-Chemie (Steinheim, Germany).

2.2. On-line coupling of the particle-into-liquid sampler with solid-phase extraction-liquid chromatography–mass spectrometry

2.2.1. Particle-into-liquid sampler

A full description of the aerosol sampling with PILS can be found elsewhere [9,14–16]. Briefly, the sampling system consists of an ADI2081 particle-into-liquid sampler (Applikon Analytical, Schiedam, The Netherlands) coupled with an eight-channel peristaltic pump (Watson Marlow 205S, Wilmington, USA). Direct Q-UV water (Millipore, USA) was used as a working liquid and for transport flow. To remove gas-phase compounds, three-channel annular denuders (242 mm length, Teflon-coated, stainless steel sheath, URG, Chapel Hill, USA) with different coatings (XAD for organic gases, potassium iodide in glycerol for ozone) were added to the sampling line and were recoated when the colour of the potassium iodide denuder changed to yellow. Aerosols were size separated before the denuder line with a cyclone (PM2.5, URG, Chapel Hill, USA), which was cleaned once a day.

During collection, the transport flow containing the aerosol sample was divided into two parts. One part was collected off-line to a pre-weighed beaker, while the other was directed to the conditioning/sampling valve of the solid-phase extraction step (see Section 2.2.4).

2.2.2. Solid-phase extraction

The selectivity of the solid-phase extraction (SPE) of acids was ensured by proper choice of the anion exchange sorbent. The tested materials were polymer-based mixed-mode anion exchange and reverse-phase (MAX) sorbent (Oasis, Waters, Milford, MA, USA) and silica-based strong anion exchange (SAX) sorbent (Isolute, IST, Mid Glamorgan, UK). For on-line coupling, a small column (30 mm × 2.1 mm I.D.) was packed in the laboratory with SAX material. Before the SAX material was used for the first time, it was treated with methanol, 100 mM acetic acid and 10 mM acetic acid. Different proportions of acids (acetic or formic) and organic modifiers (methanol or acetonitrile) were tested for desorption of the trapped analytes. Optimal loop size and solvent composition for the desorption were determined by injecting manually the mixture of standard compounds to the trap and pumping the eluting solvent through the trap directly to the mass spectrometer. Desorption was followed via extracted ion chromatograms, and the appropriate solvent volume was calculated.

After sampling, acids were removed from the trap with 500 μL of 10% acetic acid in MilliQ water by pumping HPLC eluent through the loop (see Section 2.2.4).

For the off-line extraction, solid-phase cartridges (HyperSep SAX, 100 mg/1 mL, Thermo Electron Corporation, Waltham, USA) were used with the following procedure: preconditioning (2 mL of methanol and 2 mL of MilliQ water), sample loading (amount depending on sampling time, several milliliters) and elution (1 mL of 2% formic acid in methanol). The extracts were evaporated to dryness before derivatization (see Section 2.4). The flow was kept at about 1 mL/min with the help of vacuum.

2.2.3. Liquid chromatography–ion trap mass spectrometry

Analysis was performed with a Hewlett-Packard Series 1100 liquid chromatograph (Palo Alto, USA) coupled to an Esquire 3000 plus ion trap mass spectrometer (Bruker Daltonics, USA). Electrospray ionization (ESI) in negative ion mode was used. The combination of eluents, gradient, injection volume, flow-rate and ionization parameters was optimized. Final parameters for the liquid chromatography were XBridge C18 column (4.6 mm × 75 mm, 2.5 μm, Waters Corp, USA), gradient: 0–2 min 100% of A (1% acetic acid in water), 2–5 min 50% A, 5–7.5 min 25% A, 7.5–15 min 100% B (1% acetic acid in acetonitrile), 15–20 min 100% A. Flow was 0.5 mL/min and temperature ambient. Injection volume for the direct HPLC–MS analysis was 10 μL. Parameters for the ESI-MS were capillary voltage +3600 V, end plate offset −500 V, nebulizer pressure 2.76 bar (nitrogen), 12 L/min of drying gas (nitrogen) and drying temperature 350 °C. Mass range was 50–200 amu for the first time window (0–7 min) and from 80 to 230 amu for the second (7–11 min). To ensure identification, MS^2 was used in single reaction monitoring mode for the following ions (compound and time window in parenthesis): 185 amu (*cis*-/*trans*-pinic acid, 2), 183 amu (*cis*-/*trans*-pinonic acid, 2), 187 amu (azelaic acid, 2), 201 amu (sebacic acid, 2), 167 amu (vanillic acid, 2), 165 amu (caprylic acid, 2), 151 amu (mandelic acid, 2), 149 amu (tartaric acid, 1), 147 amu (3-hydroxyglutaric acid, 1), 145 amu (adipic acid, 2), 133 amu (malic acid, 1), 121 amu