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Broad spectrum analysis of polar and apolar organic compounds in submicron atmospheric particles☆

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ABSTRACT

A method for the quantitative analysis of organic compounds on submicron particulate matter (PM_1) collected on quartz filters was developed. The compounds analyzed encompassed C_{22}–C_{35} alkanes, polycyclic aromatic hydrocarbons (PAHs), quinones, levoglucosan, cis-pinonic acid and short chain dicarboxylic acids such as malonic, succinic, glutaric, adipic, suberic, azelaic, malic and phthalic acids. The method included extraction with a pressure liquid extraction system, sample filtration though glass fibre filter, fractionation by high performance liquid chromatography and subsequent analysis by gas chromatography coupled to mass spectrometry. The study of the extraction efficiency of different solvent mixtures showed that DCM:MeOH 1:1 was the one providing the highest recoveries for all compounds. Extraction temperatures of 100 °C provided better results than 60 °C or 80 °C. This method provided comparable extraction efficiency and qualitative and quantitative data to those involving Soxhlet extraction. Method recoveries for alkanes, most PAH, quinones and polar compounds calculated from spiked real samples were 52–72%, 78–101%, 50–62% and 76–104%, respectively, reproducibilities were 2–28%, 7–29%, 10–27% and 5–28%, respectively, limits of quantification were 0.01–0.1 ng/m^3, 0.01–0.27 ng/m^3, 0.04 ng/m^3 and 0.32–2.8 ng/m^3, respectively, which affords the quantification of a broad number of primary and secondary organic constituents of submicron aerosols.

1. Introduction

Atmospheric aerosols encompass nanometric and micrometric liquid and solid particles. They are important constituents of the biosphere and have effects on climate and public health. Exposure to ambient aerosols can cause or enhance respiratory, allergic, cardiovascular and infectious diseases. These atmospheric particles may originate from a wide variety of sources, natural and anthropogenic, and processes, primary and secondary [1,2].

Primary aerosols encompass alkanes originating from epicuticular higher plant waxes or fossil-fuel residues [3], polycyclic aromatic hydrocarbons (PAHs) produced from incomplete combustion for domestic heating, energy production or vehicular traffic and polar compounds generated by vehicular traffic, meat cooking and biomass burning. Secondary aerosols are formed by atmospheric reaction of primary components with ozone, hydroxyl and nitrate radicals, which may generate of polar organic compounds such as quinones, and some dicarboxylic acids among others [4–6]. The organic composition of submicron atmospheric particles results from contributions of these primary and secondary aerosol constituents [7–10].

Submicron particles can penetrate into the membranes of the respiratory tract, enter into the blood circulation system or be transported along olfactory nerves into the brain. These particles are typically found in urban atmospheres at high concentrations [11]. They may contain PAH and PAH derivatives of known carcinogenic and mutagenic activity and polar compounds that can cause oxidative stress and other effects. Incidence rates of several health disturbances have been associated to concentrations of submicron air particulate matter and traffic-related air pollution in urban areas [12–14].

Despite previous studies on the organic chemical composition of aerosols, strong uncertainties on sources, composition, properties and mechanisms of formation still remain, namely in the submicron particles [15–19]. These unknown aspects constitute a strong handicap for the identification of specific health effects related to aerosol human exposure. Progress of understanding the etiology of these effects requires insight into the physical and chemical aerosol

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composition. This need of more information is particularly important in urban areas where human exposure to aerosols is highest.

This goal requires an increasing number of analyses at high temporal resolution. Methods allowing the determination of large numbers of compounds in efficient and simple ways are needed. Often, these methods involve an initial ultrasonic [8,10,15,20] or Soxhlet [21,22] extraction steps. Unfortunately, these extraction procedures are time consuming and require large solvent volumes, which constitute a problem for environmental disposal. Several methods have been developed, e.g. microwave, supercritical-fluid [23,24] or pressurised liquid extraction (PLE) [25–27] to reduce extraction times, solvent volumes and to improve automation. PLE is simple, fast and simplifies the steps to obtain the final extract. All these aspects have encouraged the use of this technique for the extraction of organic compounds from a variety of environmental solid matrices.

Because of the broad variety of compounds present in the aerosol samples, chromatographic fractionation is used to separate the extracts according to polarity [10,21,24,28]. Gas chromatography coupled to mass spectrometry (GC–MS) is the usual instrumental technique for determining organic compounds from low to moderate polarity in atmospheric aerosols [3,29]. However, thermally labile or low vapour pressure compounds because of highly polar functional groups must be derivatized before GC–MS analysis [30].

The present study reports the development of one of these methods using PLE [25,31,32]. Normal phase high performance liquid chromatography (HPLC) has been used to fractionate the extracts [28,33] and the fractions were analysed by GC–MS. A fast, low solvent consumption extraction method for the determination of a broad spectrum of organic compounds present in submicron atmospheric particles has been developed. It has been used for a comprehensive study of these particles in Barcelona during the cold and warm periods. Besides possibilities of identification of associations between airborne compounds and health effects, this approach also provides a strong insight into the composition of submicron aerosols.

2. Materials and methods

2.1. Reagents and analytical standards

High purity SupraSolv® acetone (AC), hexane (HX), methanol (MeOH) and UniSolv® dichloromethane (DCM) were purchased from Merck (KGaA, Darmstadt, Germany). bis-(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (BSTFA:TMCS, 99:1) were from Supelco (Bellefonte, PA, USA). Pyridine was obtained from Fluka Analytical (Steinheim, Germany).

All standards were of the highest commercially available purity (>98%): d_4-succinic acid, 9,10-anthraquinone, 9-fluorenone, levoglucosan, malonic, succinic, glutaric, phthalic, adipic, azelaic, DL-malic and cis-pinonic acids were provided by Sigma Aldrich (Steinheim, Germany). d_7-Levoglucosan was from Cambridge Isotope Laboratories (Andover, MA, USA). 1-Phenyldodecane, suberic acid and an alkane mix (from n-C_{20} to n-C_{35}) were purchased from Fluka Analytical (Steinheim, Germany). d_{10}-Pyrene, d_{50}-tetracosane, d_{10}-anthracene, d_{12}-benz[*a*]anthracene, d_{12}-benzo[*b*]fluoranthene, d_{12}-benzo[ghi]perylene and the PAH mix: acenaphthylene (Acy), acenaphtene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[*a*]anthracene (B(*a*)a), chrysene (Chry), benzo[*b*]fluoranthene (B(*b*)f), benzo[*k*]fluoranthene (B(*k*)f), benzo[*a*]pyrene (B(*a*)p), indeno[1,2,3-*cd*]pyrene (I(123-*cd*)p), benzo[*ghi*]perylene (B(*ghi*)per) and dibenz[*ah*]anthracene (D(*ah*)a) were obtained from Dr. Ehrenstorfer (Augsburg, Germany).

The standard solutions used to construct calibration curves or surrogate standards were prepared in methanol (for the polar compounds) and cyclohexane (alkanes, PAHs and deuterated PAHs). These solutions were stored at −20 °C. The BSTFA and pyridine reagents were stored at 4 °C.

2.2. Spiked samples and PM_1 samples

Airborne particles PM_1 were collected at ground level and at 40 m above ground in Barcelona (n = 56). Samples (12 h) were collected using a Digitel-DH80 Hivol-sampler (Digitel Elektronic AG, Switzerland) equipped with 150 mm diameter quartz filters 2500QAT-UP (Pallflex, Pall Corporation) at a flow rate of 30 m^3/h (total air volume of 370 m^3). The quartz filters were heated at 450 °C for 4 h to eliminate organic interferences prior to use. Before and after sampling, filters were weighed (in stable temperature and relative humidity conditions) for measurements of PM_1 mass content and stored in aluminium foil at −20 °C until analysis.

Organic compound extraction efficiency was evaluated from a series of spiked samples that were prepared by addition of the standard mixture of each pollutant family to PM_1 samples.

2.3. Pressurized liquid extraction

Filter extraction was performed by PLE using an accelerated solvent extraction instrument (ASE 150; Dionex Corporation, Sunnyvale, CA, USA) [31]. In the PLE optimized method, the filter was folded and placed into 10 mL stainless steel extraction cell. Once in the cell, the filter was spiked with deuterated standards (d_{50}-tetracosane, d_{10}-anthracene, d_{12}-benz[*a*]anthracene, d_{12}-benzo[*b*]fluoranthene, d_{12}-benzo[ghi]perylene, d_4-succinic acid, d_7-levoglucosan), to correct for potential losses during the analytical procedure and to compensate for matrix effects. Preheated glass fiber filters (27 mm, type D_{28}; Dionex, Idstein, Germany) were placed in both open sides of the extraction cells to prevent fine particles from leaving the cell and blocking the system.

PLE conditions encompass a 5 min preheat time, followed by 3 static cycles of 5 min at 1500 psi. The flush volume was 60% followed by a purge with gaseous nitrogen during 100 s. The extract was collected in a 60 mL vial. An additional rinse with the extraction solvent mixture between samples was applied to clean the system. Extraction cells were cleaned between each run by sonication with DCM and methanol (1:1, v/v) (3 × 10 min). The extracts were then filtered through a preheated (450 °C) 25 mm diameter glass-microfibre membrane filter (Sartorius, France) using a 25 mm Swinny stainless steel syringe filter holder (Sartorius, France) and a 30 mL glass syringe with Luer tip (Fortuna, Aldrich). The filtrate was concentrated by rotary evaporation to approx. 1.5 mL, transferred to a vial and further evaporated to 1 mL using a gentle stream of high-purity nitrogen.

The effect of different parameters on the extraction efficiency was evaluated including PLE cell size, extraction solvent composition, number of extraction cycles and extraction temperature. Unless otherwise noted, each extraction experiment was done in triplicate.

2.4. Sohxlet extraction

Sohxlet extractions (8 h) were carried out in an apparatus with 100 mL DCM–MeOH (2:1, v/v). The filters were spiked with standard surrogates, folded with tweezers and placed into the Soxhlet (50 mL). The extracts were filtered and concentrated as described above.