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Identification of organic compounds in atmospheric aerosol particles by on-line supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry

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Abstract

Atmospheric particles were collected with a high-volume sampling system at an urban site in Helsinki (Finland). The samples were analysed by on-line coupled supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry (SFE–LC–GC–MS). The aerosol sample was first extracted by SFE. The extract was then transferred to a liquid chromatograph where it was fractionated into four fractions according to polarity. Each fraction from the liquid chromatograph was transferred to a gas chromatograph by large-volume injection, where final separation was carried out. The first LC fraction (280 μl) contained nonpolar compounds, such as *n*-alkanes, hopanes and steranes. The second fraction (840 μl) included polycyclic aromatic hydrocarbons (PAHs) and alkyl-PAHs, while the third and fourth fractions (840 μl each) contained more polar compounds, such as *n*-alkan-2-ones, *n*-alkanals, oxy-PAHs and quinones.

Keywords: Aerosols; Air analysis; Environmental analysis; Alkanes; Polynuclear aromatic hydrocarbons; Carbonyls compounds

1. Introduction

Atmospheric aerosols are composed of a complex mixture of chemical compounds. Inhalation of airborne particles containing toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs), is of concern for public health [1,2], and identification and quantification of organic compounds in aerosol particles have been of interest for several decades. Some compounds serve as unique molecular markers of their source, and so contribute to our understanding of the air pollution cycle [3,4]. Oxidation of atmospheric organic compounds through reaction with OH radicals, ozone molecules or NO_3 radicals produces more polar and water soluble species, which play important roles in particle formation [5,6].

Unfortunately, considerable uncertainty exists in regarding to on organic aerosol data because of artefacts generated during sampling and chemical analysis [7–9]. Gas chromatography–mass spectrometry (GC–MS) is one of the most widely applied methods for the analysis and determination of aerosol composition, owing to the high separation efficiency of GC and superior identification capacity of MS. However, GC–MS analysis requires intensive sample pretreatment, including extraction of analytes, evaporation of excess solvent, filtration and fractionation. The sample pretreatment is often done manually, which can be time consuming, expensive, environmentally unfriendly and often unreliable.

Modern multidimensional chromatographic techniques are powerful analytical methods when a single chromatographic column is not sufficient to separate complex

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mixtures. Liquid chromatography coupled on-line to gas chromatography (on-line LC–GC) [10–12] and comprehensive two-dimensional gas chromatography (GC × GC) are the most powerful of those techniques [13,14].

In on-line LC–GC, the sample is cleaned, fractionated and concentrated in LC. The fraction containing the target analytes is then introduced on-line to the gas chromatograph via large-volume injection method, where several millilitres of eluent can be introduced to the GC column. In on-line LC–GC, sample pretreatment is thus carried out automatically in a closed system, minimising the problems noted above. With the large-volume injection method, on-line LC–GC offers excellent sensitivity and low detection limits. The main advantages of the GC × GC technique are the increased peak capacity and sensitivity. Very complex mixtures can be analysed in a single run. However, in GC × GC, the sample preparation is typically carried out off-line.

The multidimensional chromatographic methods are useful in atmospheric analysis because the target analytes are typically present in trace levels (less than ng/m^3) in very complex sample matrix. Both LC–GC and GC × GC methods have been reported for the atmospheric analysis. LC–GC with on-column interface [15] and programmed temperature vaporiser [16] have been successfully applied for analysis of polycyclic aromatic compounds in atmospheric particles collected by a high-volume sampler. On-line coupled supercritical fluid extraction–gas chromatography (SFE–GC) has been used for analysis of relatively volatile organic compounds in aerosol samples [17]. GC × GC techniques have been applied for analysis of volatile organic compounds [18] and semi-volatile organic compounds [19,20] collected from atmosphere.

Coupling of multidimensional techniques to sample extraction methods further decreases the manual sample pretreatment steps required. Pressurised hot water extraction has been coupled to LC–GC for analysis of PAHs and brominated flame retardants in sediment samples [21,22]. Ericsson and Colmsjö [23] have analysed organophosphate esters from atmospheric samples by microwave-associated extraction coupled with solid-phase extraction and gas chromatography. Recently, an on-line coupled supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry (SFE–LC–GS–MS) system was developed and applied for determination of atmospheric PAHs levels in urban Helsinki area [24]. The same system was used to analyse atmospheric organic acids, applying in situ derivatisation in SFE [25].

Here we extended the SFE–LC–GC–MS method to the characterisation of organic aerosol components, such as *n*-alkanes, hopanes, steranes, PAHs, oxy-PAHs, *n*-alkanals and *n*-alkan-2-ones. The previously developed method was further optimised to allow more efficient extraction of also relatively polar compounds and LC fractionation of the extract according to polarity of the analytes. Aerosol samples were collected by high-volume sampler with quartz filter at an urban site in Helsinki (Finland) during summer 2002.

2. Experimental

2.1. Sampling

Sampling was carried out on the roof of the Department of Physical Sciences, University of Helsinki (60°12′N, 24°58′E and 50 m above sea level) in a location where the major emission source of pollutants is traffic. The sampling site is about 6 km north-east of the city centre and about 200 m away from a busy road that feeds to a major motorway. Small patches of forest nearby contribute minor biogenic emissions. There is also a bay west of the sampling site, which may act as a biogenic emission source. Average weekday traffic at the entrance to the motorway for the year 2001 was 53,000 vehicles per day. The corresponding number of heavy vehicles at the same site was 5500, of which full and semi-trailers accounted for 1660.

Aerosol samples were collected on Munktell MK360 240-mm quartz microfibre filters (Munktell, Grycksbo, Sweden). The filters were baked at 880 °C for 5 h and kept in a clean dessicator until sampling. Air was drawn at 100 m^3/h through the filters with a high-volume sampler. No special devices were used for removal of gaseous oxidants, such as ozone and OH radicals, or for collection of volatilised particulate compounds. After the sampling, the filters were kept in a clean dessicator at 4 °C in dark until chemical analysis. Analysis was carried out within one week of the sampling.

2.2. Chemicals and reagents

SFE-grade CO_2 was from Messer Suomi (Vantaa, Finland). HPLC-grade *n*-hexane and dichloromethane were purchased from J.T. Baker (Deventer, The Netherlands), and ethyl acetate was from Labscan (Dublin, Ireland). *n*-Hexane was further distilled in our laboratory. A PAH mixture (Z-014G-R) containing 17 compounds in CH_2Cl_2–benzene (1:1, v/v) was obtained from AccuStandard (New Haven, CT, USA). *n*-Alkanes with even carbon number (C_{12}–C_{32}) were from Fluka (Steinheim, Switzerland). An internal standard, 1,1′-binaphthyl, was purchased from Acros Organics (Geel, Belgium). Anthraquinone, 2-methylanthraquinone, acenaphthenequinone, 9-fluorenone, 5,12-naphthacenequinone, phenanthrene-9-carboxaldehyde and xanthone were from Fluka. All standards were diluted to desired concentrations with *n*-hexane–ethyl acetate mixture (95:5, v/v).

2.3. SFE–LC–GC–MS

Schematic diagrams of the SFE–LC–GC–MS system with different valve positions are shown in Fig. 1. The SFE was a Suprex Prep Master with Accutrap unit (Pittsburgh, PA, USA). Only the relevant parts of the SFE unit are shown in the figure. The SFE consisted of a dual-piston pump, an oven, a 3-ml laboratory-made extraction vessel, a multiple port valve, a computer-controlled needle pressure restrictor (R) and a solid-phase trap. The solid-phase trap (8.0 cm ×

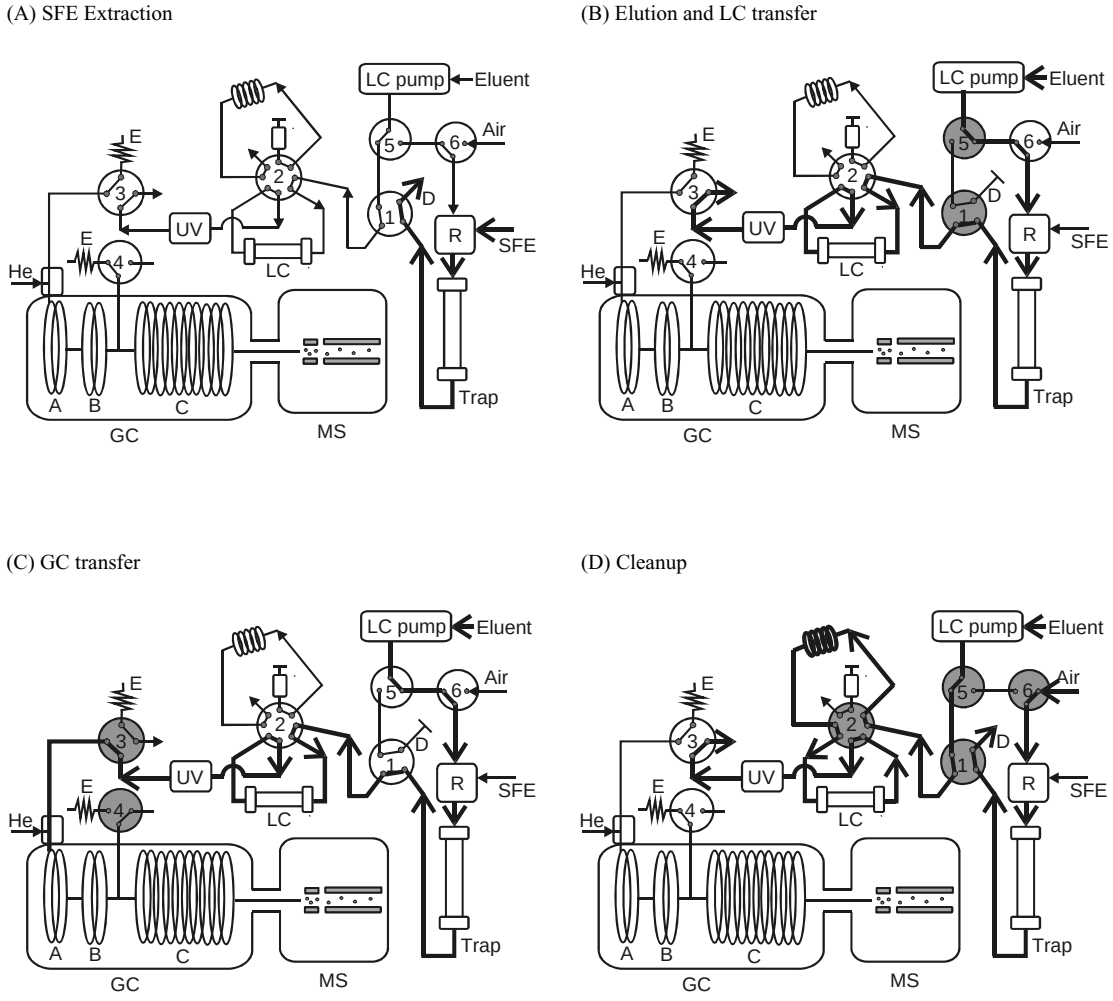

Fig. 1. SFE–LC–GC–MS system for different multi-port valve positions. A, SFE extraction; B, elution and LC transfer C, GC transfer; D, cleanup; E, restrictor; R, pressure restrictor. Switched valves are indicated by the darkened colour.

2.1 mm i.d.) was packed with 0.5 g octadecylsilane particles with diameter of 60 μm (J & W Scientific, Folsom, CA, USA).

The LC system consisted of a 15.0 cm × 2.0 mm i.d. Luna silica column packed with particle of 5 μm diameter (Phenomenex, Torrance, CA, USA), a Jasco UV-970 detector (Jasco, Tokyo, Japan) and a pump (PU-980, Jasco). The tubings for the SFE unit were made of stainless steel of dimensions 1/16 in. o.d. and 0.5 mm i.d. (1 in. = 2.54 cm; VICI Valco, Schenkon, Switzerland); polyether ether ketone (PEEK) tubings of the same dimension (Alltech, Lokeren, Belgium) were used for LC. The interfaces between the solid-phase trap and Valve 1 and the loop on Valve 2 were made of PTFE (1/16 in. o.d. and 0.5 mm i.d., Alltech). All multiple port valves were purchased from VICI Valco.

A thin silica capillary (Composite Metal Services, Hallow, UK, 50 cm × 100 μm i.d., 170 μm o.d.) was passed from Valve 3 through the on-column injector to a precolumn (A) in the gas chromatograph, HRGC 5300 (Carlo Erba Instrumentation, Milan, Italy). The precolumn consisted of a 10 m × 0.53 mm i.d. deactivated fused silica column, A (Agilent Technologies, Karlsruhe, Germany), that was connected by a pressfit connector to a 3 m × 0.32 mm i.d. retaining precolumn, B (HP-5, 0.25 μm film thickness, Agilent Technologies). The retaining precolumn was further connected by a Y-piece pressfit to a solvent vapour exit (Valve 4) and the analytical column, C (HP-5, 20 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies). The capillary between the Y-piece pressfit and Valve 4 was wider (0.53 mm i.d.) to accelerate the solvent vapour discharge. Pressfits were purchased from BGB Analytik (Zürich, Switzerland). The carrier gas, helium, was introduced from the side of the on-column injector. Capillary restrictors (E; Composite Metal Services, 1 m × 50 μm i.d.), mounted on Valves 3 and 4, allowed a small purge flow of the carrier gas to flow out very slowly during the GC analysis to prevent the remainder of the solvent from reaching the detector.

The interface between the GC system and the quadrupole MS system (Automass Solo, Thermoquest, Argenteuil, France) was maintained at 300 °C and the ion source at 250 °C. Electron impact ionisation was done at 70 eV and positive ions were monitored from 50 to 500 amu. The MS

system was operated by and the data analysed with Xcalibur software.

2.4. Identification and quantification

Identification and quantification were done with authentic standards, if available. When a particular compound could not be obtained, identification was based on comparison of retention order with *n*-alkanes or PAHs found in the literature, comparison with mass spectral libraries and fundamental interpretation of mass spectra. Quantification of odd-carbon *n*-alkanes was carried out using adjacent even-carbon *n*-alkanes.

2.5. Analytical procedure

Before analysis, all valves were set at loading position (Fig. 1A). The extraction vessel was filled with the filter sample cut into small pieces, 10 μl of the internal standard (5 μg/ml) and 400 μl of dichloromethane (modifier), and the vessel was placed in the oven. SFE conditions were adjusted to 400 atm and 150 °C (1 atm = 101,325 Pa). The SFE was carried out in two steps with static mode (10 min) followed by dynamic mode (45 min and flow rate 1.5 ml/min). The pressure restrictor was kept at 80 °C. The analytes were trapped in a solid-phase trap, which was maintained at 10 °C during the extraction.

When the extraction was over, the pressure restrictor was cooled down, and Valve 5 was switched to start the elution with *n*-hexane–ethyl acetate (95:5, v/v) at the flow rate of 210 μl/min. The exhaust (D in Fig. 1) was blocked by a back-pressure restrictor so that when the eluent pushed the gas remaining in the solid-phase trap to the exhaust a low pressure was build up in the system. The low back-pressure ensured that no dry channels would be left in the trap. When the front of the eluent reached Valve 1, the valve was switched to inject the sample to the liquid chromatograph, where fractionation was carried out, as shown in Fig. 1B.

When the fraction of interest was observed by the UV detector, Valves 3 and 4 were switched for injection to the GC as shown in Fig. 1C. The eluent was evaporated by partially concurrent solvent evaporation technique and discharged with helium through Valve 4 at oven temperature 80 °C and 1.3 bar inlet pressure. Under these conditions, most of the eluent was discharged via SVE, while the analytes were successfully trapped and concentrated on the precolumn. When the transfer of the fraction was complete, Valve 3 was closed and the LC pump was stopped. Valve 4 was kept open for a further 15–30 s to ensure elimination of most of the eluent, and the GC analysis was started when the pressure in the ion source returned to normal level. The GC temperature programme was as follows: 80 °C (1 min), 15 °C/min; 150 °C, 5 °C/min; 200 °C, 10 °C/min; 300 °C (30 min). After the GC analysis, the following fraction was transferred by starting the LC pump and opening Valves 3 and 4.

When the analysis was complete, the solid-phase trap was rinsed with the eluent and dried with clean compressed air by turning Valve 6. The LC column was cleaned with dichloromethane (500 μl) kept in the loop on Valve 2. The flow of the eluent during the LC column rinse was reversed for more effective cleaning. The solid-phase was dried with clean compressed air by switching Valve 6. The valve configuration is shown in Fig. 1D. After the cleaning procedure, the instrument was ready for the next analysis.

3. Results and discussion

SFE is often more selective than conventional liquid extraction methods, such as Soxhlet extraction, while still maintaining good efficiency. This is mainly due to the possibility to tune the solvent properties of supercritical fluids to better match the analytes and because of the good physical properties of the fluid. This is especially true for supercritical CO_2 extraction of nonpolar analytes in solid samples containing polar matrix compounds.

SFE most effectively extracts compounds that are nonpolar with relatively low boiling points. In the best case, the SFE extracts can be injected directly to a gas chromatograph. In aerosol analysis, however, the most abundant compounds are nonpolar mixture of branched, cyclic and unsaturated hydrocarbons, generally characterised as an unsolved complex mixture (UCM) [26,27]. The UCM generates a large hump in the gas chromatogram, obscuring the peaks of other trace compounds. Direct GC separation and identification of the trace compounds become difficult, therefore.

SFE followed by on-line coupled LC provides a separation of the SFE extracts in terms of polarity. Interpretation of the results becomes easier because the number of peaks in gas chromatograms is decreased, and some of the overlapping of peaks can be avoided. In addition, peak identification and quantification with MS become more reliable because of lower background noise in the spectra.

3.1. SFE conditions

Addition of a modifier to CO_2 is known to enhance the recovery of polar analytes in SFE. Dichloromethane was chosen as modifier because of proven effectiveness [28] and because it is compatible with LC–GC. Dichloromethane (400 μl) was directly added to the extraction vessel (3 ml), and static mode extraction was carried out for 10 min (400 atm, 150 °C). After the static extraction, dynamic extraction was carried out with the conditions already optimised for PAHs, i.e. 400 atm and 150 °C for 45 min at 1.5 ml/min flow rate measured at the pump [29].

If the solid-phase trap becomes saturated with the modifier, breakthrough of analytes and lower recovery may result. One way to avoid this problem is to keep the temperature of the solid-phase trap above the boiling point of the modifier [30]. A test performed with solid-phase trap temperatures

of 10 and 40 °C, however, showed no significant difference in recoveries of the analytes. Owing to its low boiling point and the high flow rate of CO_2, dichloromethane probably passed through the trap as vapour even at 10 °C. Thus, 10 °C was chosen as the temperature for the solid-phase trap to maximise the collection efficiency of the analytes.

3.2. LC–GC conditions

The removal of eluent from the LC–GC system was carried out by on-column interface with partially concurrent eluent evaporation technique. This technique is one of the best eluent evaporation techniques for LC–GC if volatile compounds are analysed [10]. Quantitative results were obtained for compounds less volatile than C_{14}-alkane for the transfer conditions at 80 °C with inlet pressure at 1.3 bar (helium).

Fractionation with pure *n*-hexane made the normal-phase LC fractionation unstable due to moisture present in the air or in the sample. The fraction volumes were also too large to be transferred to the gas chromatograph. Polarity of the eluent was increased by addition of ethyl acetate. 5% (v/v) ethyl acetate showed the optimum conditions for elution of the analytes from the solid-phase trap and fractionation of the analytes in LC. Elution with *n*-hexane containing more than 5% ethyl acetate, on the other hand, resulted in overlapping of the fractions of *n*-alkanes and PAHs.

A crude fractionation occurred already in the elution of the solid-phase trap. If necessary, some compounds can be avoided from entering to the LC–GC system by letting the part of the elute flow to exhaust on Valve 1 before it is switched for LC transfer. This procedure is useful, if aerosols contain a large amount of nonpolar compounds are liable to overload the LC column.

3.3. Quantitative analysis

In quantitative analysis, the peak areas of analytes were first corrected with recovery standard, and the concentrations were then calculated using the calibration curves. In the calculation, reconstructed ion chromatograms were used with the selective ions. The calibration curves were made for even-carbon *n*-alkanes, PAHs and a few oxy-PAHs at concentrations ranging from 2 to 100 ng. The regressions for the calibration curves were better than 0.98. Limits of determination ($S/N > 3$) ranged from 0.03 to 0.06 ng for PAHs. Limits of determination for *n*-alkanes were higher (~2 ng) due to the noisier baseline of the alkane fraction. Relative standard deviations of repeated analyse of the same filter sheet typically ranged from 8 to 18% for PAHs ($n = 4$).

3.4. Quality of filter material

It is common to bake filters before sampling to remove organic impurities. Furthermore, even SFE-grade CO_2 contains small amounts of contaminants, such as hydrocarbons. Owing to its highly efficient concentration steps, the SFE–LC–GC–MS system often showed peaks caused by contaminants. Thus, blank tests were carried out to examine the effect of contaminants in CO_2 and the filters. Fig. 2 shows the contamination levels measured in an empty extraction vessel, an extraction vessel containing filters without oven treatment and an extraction vessel containing filters baked at 880 °C for 5 h. After the filters were baked, they were removed from the oven at 200 °C, and immediately transferred a clean extraction vessel. The degree of contamination was determined by comparing the peak areas with those of typical aerosol analysis.

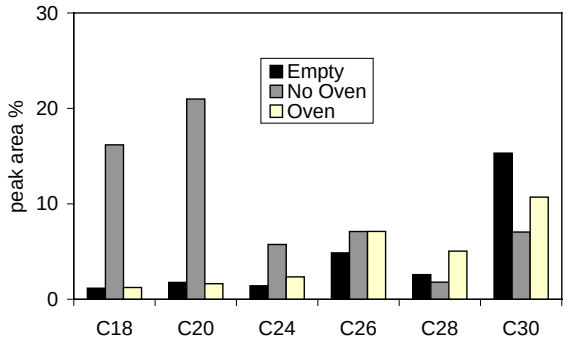

Fig. 2. *n*-Alkane blank analysis of empty extraction vessel (Empty), extraction vessel with filters without oven treatment (No Oven) and extraction vessel with filters with oven treatment (Oven). The peak areas are shown relative to those of aerosol samples ($n = 5$).

The results showed that the untreated filters were contaminated by light *n*-alkanes (C_{18}–C_{24}) but that they were efficiently removed by baking of the filters. The oven-treated filters showed similar levels of light *n*-alkane to those of the empty vessel. The light *n*-alkanes in the empty extraction vessel in fact originated from SFE-grade CO_2. Contamination with the heavier *n*-alkanes (C_{26}–C_{30}) was also caused by CO_2, and thus no significant differences were seen whether the filter was baked or not. In ambient air, *n*-alkanes up to C_{25} tend to be present in the gas phase [31]. This suggests that untreated filters are usually contaminated with gas-phase compounds.

This finding needs to be taken into account especially since the repeated blank analyse sometimes gave different results. Degree of contamination, of course, is not consistent for filters. Furthermore, the capacity of quartz filters to adsorb gaseous compounds can vary significantly even for filters with the same product number [32].

3.5. Aerosol analysis

Fig. 3 shows a typical liquid chromatogram for an aerosol sample (wavelength 254 nm). The fractionation was fairly crude because the analytes arrived at the LC as a broad initial band from elution of the solid-phase trap. The SFE extract was separated into four fractions, which were transferred to the gas chromatograph one at a time, and gas chromatograms are shown in Fig. 4 (total current ion). Table 1 summarises the identified compounds.

Table 1
Organic compounds found in aerosols collected in Helsinki with a high-volume sampler

	t_R (min)
Fraction 1 (fraction volume, 280 μl)	
n-Alkanes[a] (C_{16}–C_{42}) (2.9–16.3 ng/m^3)	
Hopanes (C_{28}–C_{35})	
Steranes (C_{27}–C_{29})	
Fraction 2 (fraction volume, 840 μL)	
Dibenzofuran	7.5
Fluorene[a] (0.009 ng/m^3)	7.78
Dimethylbiphenyl	8.4
Phenanthrene[a] + anthracene[a] (0.14 ng/m^3)	10.7
Fluoranthene[a] (0.20 ng/m^3)	15.6
Pyrene[a] (0.19 ng/m^3)	16.5
Retene	20.1
Benzo[*a*]anthracene[a] + chrysene[a] (0.35 ng/m^3)	21.1
Triphenylene	22.2
Benzo[*b*,*k*]fluoranthene[a] (0.20 ng/m^3)	24.1
Benzo[*a*]pyrene[a] (0.24 ng/m^3)	24.7
Indeno[1,2,3-*cd*]pyrene[a] (0.049 ng/m^3)	27.4
Benzo[*ghi*]perylene[a] (0.17 ng/m^3)	27.7
Dibenzo[*a*,*h*]anthracene[a] (0.12 ng/m^3)	28.4
Coronene	34.4
Methyl- and dimethyl-PAHs	
Fraction 3 (fraction volume, 840 μl)	
Verbenone[a] (0.17 ng/m^3)	3.5
Methyl-1-methylethylphenol[b]	4.2
9-Fluorenone[a] (0.03 ng/m^3)	10.1
Methyl-9-fluorenone	12.3
Phthalic acid ester	13.8
Anthraquinone[a] (0.21 ng/m^3)	14.2
4*H*-Cyclopenta[*def*]phenanthren-4-one	15.3
Methylanthraquinone[a] (0.59 ng/m^3)	16.5
Methyl-4*H*-cyclopenta[*def*] phenanthren-4-one[b]	17.0
Dibenz[*b*,*e*]oxepin-6,11-dione	18.1
Benzofluorenones[b]	20.2
7*H*-Benzo[*de*]anthracen-7-one[a] (0.61 ng/m^3)	20.3
Anthracene- or phenanthrene-dicarboxylic anhydride	21.0
Trimethylfluoranthene/trimethylpyrene[b]	21.9
2,12-Naphthacenequinone[a,b] (0.14 ng/m^3)	22.4
Benzopyrenone	24.0
7*H*-Benzo[*hi*]chrysen-7-one	25.1
5*H*-Chryseno[4,5-*bcd*]pyran-5-one[b]	25.5
Dibenzo[*def*,*mno*]chrysene-6,12-dione[b]	28.3
n-Alkanals (C_{24}–C_{32})	
n-Alkan-2-ones (C_{19}–C_{31})	
Fraction 4 (fraction volume, 840 μl)	
Chloroxanthen-9-one[b]	13.0
4-Hydroxy-9-fluorenone[b]	13.8
Xanthone[a] (0.09 ng/m^3)	13.8
Phthalic acid ester	13.8
Methyl-9-fluorenone	14.0
Anthraquinone[a,c]	14.2
2-Nitrofluorene (?)	15.2
Methylanthraquinone[a,c]	16.5
Phenathrenecarboxaldehyde[a] (0.04 ng/m^3)	16.7
Anthracenecarboxaldehyde	16.9
9-Nitroanthracene (?)	17.4
4-Oxapyren-5-one[b]	17.4
7*H*-Benzo[*de*]anthracen-7-one[a,c]	20.3
Anthracene- or phenanthrene-dicarboxylic anhydride[c]	21.0
Oxabenzo[*a*]anthracenone[b]	22.3
Benzopyrenone	24.9

LC fractions 1–4 are of increasing polarity. t_R: retention time (min). Other compounds identified only tentatively with MS and literature.
[a] Mass spectral identification confirmed with authentic standards and their retention times.
[b] Can be an isomer or other very similar compound.
[c] Peak overlapped with the one in fraction 3. Concentrations given (in fraction 3) are the sum of two peaks.

It is evident from the gas chromatograms that the fractionation of the mixture of nonpolar compounds (fraction 1) and more polar compounds (fraction 2) was successful with the LC conditions used in this study. The large peaks at the identical retention times on gas chromatograms for fractions 2, 3 and 4 were caused mainly by phthalate compounds. The compounds found in each fraction are specified below.

The sample described in Table 1 was collected for 24 h on 9 July 2002. During the sampling, the temperature ranged from 16 to 20 °C (average 18.9 °C) with relative humidity from 30 to 80% (average 64.5%). Precipitation was zero. The weather was stable with pressure 1022.1 mbar with maximum global radiation of 764 w/m^2. Nights in Helsinki are short in summer, and the global radiation was zero only for 3 h. The wind was weak (2 m/s), mainly from 144 to 250°.

3.5.1. Fraction 1

Fraction 1 (LC retention time 2:55–4:15, 280 μl) contained nonpolar compounds that were not retained by the silica column. The gas chromatogram of this fraction showed the wide hump, characteristic of an as unresolved complex mixture (UCM).

n-Alkanes from C_{16} to C_{42} were identified with $m/z = 85$ and 99. Total *n*-alkane concentration from C_{18} to C_{34} was 128 ng/m^3 with $C_{max} = C_{23}$ (16.3 ng/m^3) and $C_{min} = C_{29}$ (2.9 ng/m^3). Concentrations for odd *n*-alkanes were

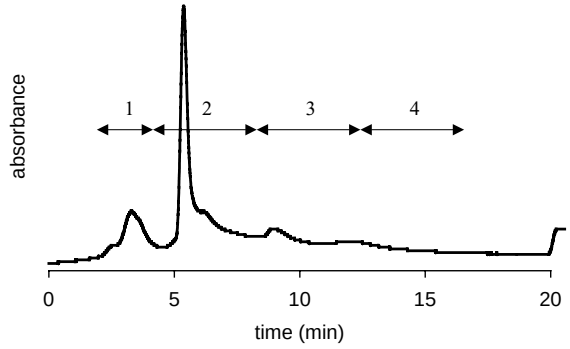

Fig. 3. Liquid chromatogram of an aerosol sample (UV at 254 nm). Separation was carried out by isocratic elution with *n*-hexane containing 5% (v/v) ethyl acetate at flow rate 210 μl/min. The numbers in the figure refer to the fractions transferred to the gas chromatograph.

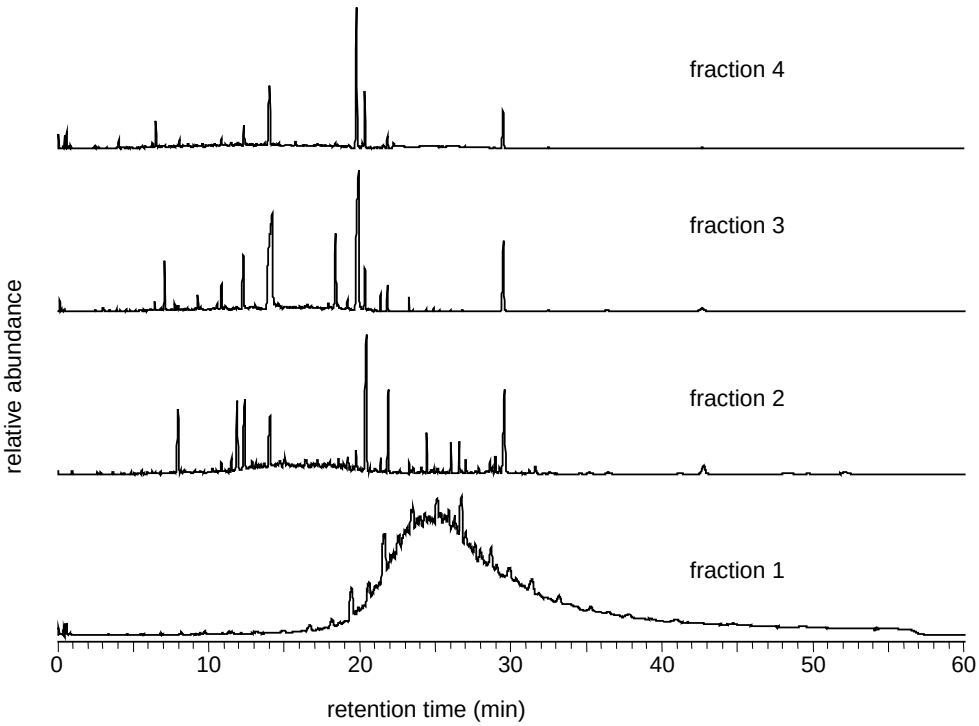

Fig. 4. Gas chromatograms (total current ion) of the fractions separated in LC. The intensity of peaks are expressed as relative abundance for each chromatogram.

calculated from using calibration curves of adjacent even *n*-alkane standards. The distribution pattern of *n*-alkanes was similar but the concentration levels slightly below the levels observed in urban areas elsewhere [33–35]. The concentrations of *n*-alkanes were higher between C_{20} and C_{26} (average 9.7 ng/m^3) than between C_{26} and C_{34} (average 5.3 ng/m^3). The carbon preference index (CPI) was 1.5 (C_{18}–C_{35}). The biogenic signature of the *n*-alkane homologue distribution typically exhibits $C_{max} > C_{27}$ with CPI > 3, whereas the petrogenic signature at C_{max} is less than C_{26} with CPI close to unity [35–37]. The source of the *n*-alkanes at the sampling site was, therefore, anthropogenic and natural with the anthropogenic source dominant.

Hopanes from C_{28} to C_{35} ($m/z = 191$) and steranes possibly from C_{27} to C_{29} ($m/z = 218$) were identified [38–40]. The hopanes and the steranes are molecular fossils present in crude petroleum and subsequently in lubricating oil, diesel fuel, road dusts and tyre debris [36,41]. Traffic is thus a very important emission source for the compounds found at the sampling site. At the same time, air mass back trajectory calculations indicated that the air mass over Helsinki at the sampling time came from urban areas in Estonia, southern Sweden, Denmark, north-western Germany and the Netherlands (see Fig. 5). Thus, a part of the observed organic compounds may be long-range transported rather than local in origin.

3.5.2. Fraction 2

The second fraction (4:15–8:15, 840 μl) contained mainly PAHs and alkyl-PAHs, identified with reference to authentic standards and with the aid of the literature [42,43]. The concentrations of PAHs ranged from 0.009 ng/m^3 (fluorene) to 0.049 ng/m^3 (indeno[1,2,3-*cd*]pyrene) and are comparable with those recorded in our previous study [24] and slightly lower than those observed in other European urban centres [44,45].

The concentration ratio of fluoranthene to the sum of fluoranthene and pyrene can be used as a source apportionment. The value obtained in the present study was 0.52, which reflects the importance of vehicular emissions in the sampling area [46–50]. Indeed, PAHs and alkyl-PAHs are emitted in significant amount by gasoline- and diesel-powered vehicles [26,36,51]. The value obtained in this study must be interpreted with caution, however, because both fluoranthene and pyrene are sensitive to gas–particle partition and can be oxidised in the atmosphere or during sampling.

Methyl- and dimethyl-PAHs often showed two or three peaks adjacent to each other, depending on the position of the methyl group.

3.5.3. Fraction 3

Fraction 3 was taken from 8:15 to 12:15 in LC retention time (840 μl), and contained more polar or larger compounds, such as trimethyl-PAHs, oxy-PAHs, *n*-alkanals and *n*-alkan-2-ones.

Some of the oxy-PAHs identified in this fraction are formed typically during fuel combustion [51,52], and they appear in urban organic aerosols [47,48,53]. Other oxy-PAHs are formed in the atmosphere or on the quartz filter through oxidation reactions of parent PAHs. Benz[*a*]

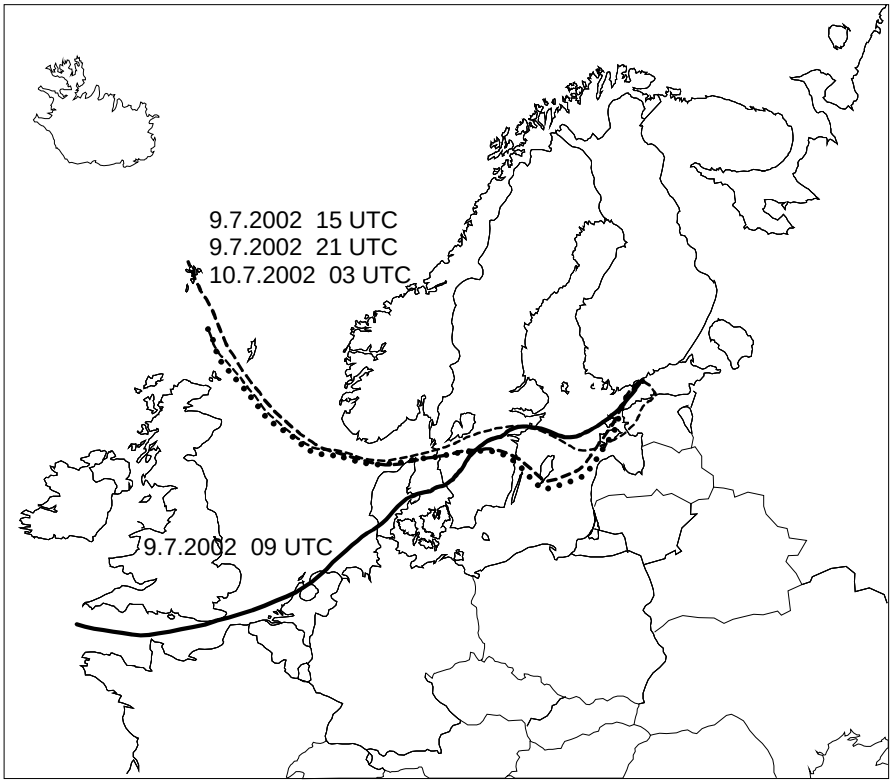

Fig. 5. Five days long air mass back trajectories arriving at Helsinki 50 m above mean sea level. The trajectories were calculated using 1° grid weather data from the European Centre for Medium-Range Weather Forecasts (http://www.ecmwf.int/).

anthracene-7,12-dione and 7*H*-benz[*de*]anthracene-7-one are good examples of such compounds [49].

Homologue series of long chain ketones and aldehydes (*n*-alkan-2-ones and *n*-alkanals) were identified according to their retention data and with *m*/*z* 58 and 82 [40,50,54]. *n*-Alkan-2-ones were detected from C_{19}–C_{31} ($C_{max} = C_{27}$) with an odd-to-even relationship, but *n*-alkanals from C_{24}–C_{32} ($C_{max} = C_{28}$) with an even-to-odd relationship. *n*-Alkan-2-ones are considered to originate through in situ microbial oxidation of *n*-alkanes, and *n*-alkanals are likely to originate from biogenic sources [37,49,54]. The concentrations of those compounds were much lower than those of *n*-alkanes, however.

3.5.4. Fraction 4

Fraction 4 (LC: 12:15–16:15, 840 μl) contained most polar compounds of the four fractions and some compounds that overlapped with fraction 3. Most of the compounds in this fraction were secondary oxidation products of nonpolar compounds. The gas chromatogram of this fraction did not contain as many peaks as the previous fractions. Analysis by SFE–LC–GC–MS becomes less quantitative as the polarity of the analytes increases. Supercritical CO_2 with 400 μl modifier (dichloromethane) is not efficient for the extraction of polar compounds, and the LC column retains strongly polar compounds, especially those containing OH functional groups. Our attempt to recover *n*-alcohols by back-flushing the LC column with dichloromethane proved unsatisfactory (less than 5% recovery). As shown for carboxylic acids [25], derivatisation during SFE can be successfully employed for the polar analytes.

4. Conclusions

The SFE–LC–GC–MS method enabled analysis of aerosol particles semi-automatically in a closed system, eliminating the manual sample pretreatment procedure that is often time consuming, environmentally unfriendly and liable to generate errors. SFE was easy to couple on-line with LC–GC, and the compatibility between the techniques was excellent for non- and semi-polar compounds. Further fractionation by LC and large-volume sample introduction to the GC system produced excellent sensitivity and low limits of detection, both essential for the analysis of atmospheric samples.

The air at the sampling site was polluted mainly by anthropogenic activities, and the pollution level, measured by PAH concentrations, was similar to that of other European cities. The CPI value calculated from the *n*-alkane series confirmed the importance of anthropogenic emission sources at the sampling site. The identification of *n*-alkanals and *n*-alkan-2-ones as well suggested that biogenic emission sources play a minor role in the sampling area.

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