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Comprehensive two-dimensional gas chromatography in the analysis of urban aerosols

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Abstract

Comprehensive two-dimensional gas chromatography utilising a semi-rotating cryogenic modulator was applied to the analysis of urban aerosols. Samples were collected onto glass fibre filters using a high-volume sampler in Helsinki, Finland. Sample preparation included extraction into *n*-hexane–acetone mixture and clean-up on silver-impregnated silica column. Analyses were performed with GC × GC–FID and GC × GC–QMS equipment. Linearity of the method was good with R^2 values greater than 0.994 for all analytes. Polycyclic aromatic hydrocarbons (PAHs) and oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) were identified and quantified in urban particulates. PAH and oxy-PAH concentrations ranged from 0.5 to 5.5 ng/m^3.

Keywords: Organic aerosols; Air analysis; Gas chromatography, comprehensive two-dimensional; Polycyclic aromatic hydrocarbons; Oxygenated polynuclear aromatic hydrocarbons

1. Introduction

Atmospheric aerosol particulates have numerous effects on climate, health and the environment. To name of a few, they affect the climate directly by scattering or absorbing the incoming solar radiation and indirectly by acting as cloud condensation nuclei. Atmospheric particulates are classified into fine (diameter $\leq$ 2 μm) and coarse (diameter $>$ 2 μm) fractions, which have different sources, lifetimes and effects. The access of the fine particulates to the alveoli of the lungs is an important health issue.

The carbonaceous fraction of the atmospheric particulate matter contains elemental carbon and a large number of organic compounds with different solubilities, reactivities and physical properties [1]. Two important groups of semivolatile organic compounds are polycyclic aromatic hydrocarbons (PAHs) and oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs), which are formed in combustors through incomplete combustion of organic matter such as fossil fuels and wood, and are directly emitted to the lower atmosphere as primary aerosols. Oxy-PAHs are also formed in the atmosphere through photooxidation of parent PAHs [2]; i.e. they are formed as secondary aerosol. Some PAHs and oxy-PAHs have mutagenic and carcinogenic properties [3].

Particulate PAHs and oxy-PAHs have been collected onto filters using high volume air samplers

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[4,5] or alternatively by size-segregated impactors [6,7] when the size distribution was an interest. Vapour-phase PAHs and oxy-PAHs have been trapped with a polyurethane foam (PUF) attached to the sampler [8,9]. Sample pre-treatment usually includes sonication or Soxhlet extraction with organic solvent followed by a fractionation step that separates aliphatics from the more polar components [4,10,11]. The analysis of PAHs is usually carried out by gas chromatography–mass spectrometry (GC–MS) but also liquid chromatography (LC) with a fluorescence detection has been used [12]. Because of the complexity of the samples also multidimensional techniques such as on-line coupled LC–GC and supercritical fluid extraction (SFE) on-line coupled to LC–GC–MS have been applied as well [13–15].

A new multidimensional technique, comprehensive two-dimensional gas chromatography (GC × GC), was introduced in 1991 [16]. The GC × GC technique utilises two different gas chromatographic columns with a modulator placed between. In contrast to conventional multidimensional analysis in which only one or few fractions are transferred from the first to the second column, in GC × GC, the whole sample is subjected to the second-column separation. The modulator collects a small fraction of the solute stream eluting from the first column and introduces it to the second column. The modulator works continuously through the analysis and the duration of the collection is typically 2–10 s. Of several types of modulators in use the cryogenic ones are the most popular. For recent reviews of the modulators, see [17,18]. In GC × GC, the first column is usually a long non-polar column, in which separation is mainly based on the volatility of the components. The second column typically has thin (film thickness of 0.1 μm) polar or semi-polar stationary phase and analytes are separated according to their polarity. The inner diameter of the second column is usually only 0.1 mm, while the length varies between 0.5 and 2 m. As a result of small dimensions the analysis in the second column is faster than that in the first column and the modulation time (i.e. duration of the collection) can be kept very short. Peaks eluting from the second column are very narrow, typically 50–200 ms wide, which sets demands on the detection. Sampling rates between 50 and 200 Hz are favoured.

The main advantage of the GC × GC technique is the increased peak capacity which resulting from the orthogonal separation [19,20]. A further feature of the GC × GC technique is an ordered structure of the chromatograms [21,22]. The first GC × GC applications were mostly involved the analysis of petrochemical products, but the application range has widened during the last three or four years. Recently, for example, environmental [23,24], food [25–27] and essential oil [28] samples have been analysed by GC × GC.

The present paper describes a GC × GC method for the analysis of particulate polycyclic aromatic hydrocarbons (PAHs) and oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs). Compounds were identified by GC × GC–FID and GC × GC–QMS instrumentation, while the quantification was carried out with GC × GC–FID equipment.

2. Experimental

2.1. Chemicals

All solvents were HPLC grade and except *n*-heptane were purchased from Lab Scan Analytical Sciences Ltd. (Dublin, Ireland). *n*-Heptane was from Fisher Scientific Ltd. (Loughborough, UK). A PAH mixture (Z-014G-R) containing 17 components was purchased from AccuStandard, Inc. (New Heaven, CT, US). The compounds in the mixture were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene and dibenzo(ah)anthracene. A diesel range hydrocarbon mixture (DRH-001S-10X) containing even-numbered *n*-alkanes from decane to octacosane was also from AccuStandard, Inc. Individual oxy-PAH standards were from Fluka (Buchs, Switzerland) and they were (−)-verbenone, 9H-fluorenone, xanthone, acenaphthenequinone, 9,10-anthracenedione (anthraquinone), 2-methylanthraquinone, phenanthrene-9-carboxaldehyde, 7H-benz(de)anthracen-7-one and 5,12-naphthacenedione. Stock solutions were prepared in toluene and further diluted to the desired concentrations with *n*-hexane. The recovery standard, 2,2′-binaphthyl, was purchased from AccuStandard, Inc. and the quantification standard, 4,4′-dibromooctafluorobiphenyl, from Aldrich (Gillingham, UK).

2.2. Sampling and sample preparation

Atmospheric particulate samples were collected onto glass fibre filters (∅ 240 mm, Munktell, Grycksbo, Sweden) with a high volume sampler at a flow rate of 90 m^3/h. Before use, the filters were baked at 480 °C for 8 h. The sampling site was located near the centre of Helsinki at the Kumpula campus of the University of Helsinki. The sampler was placed on the roof of the building for Physical Sciences (60°12′N, 24°58′E) approximately at 40 m height. Near the sampling site there is a busy road, a residential area, some forest and, at the time of sampling, a construction site for new campus buildings. A bay in Baltic Sea lies about 1 km to the east. The sampling period was 24 h, from noon to noon. After sampling, the filters were stored in a freezer until sample preparation and analysis.

Silver impregnated silica [29] was used in the sample clean-up. Briefly, a slurry containing 10% (w/w) $AgNO_3$ solution and silica was prepared and dried in an oven at 120 °C. An empty column (20 mm × 2.1 mm i.d.) was filled with the dried silica particles and *n*-heptane was pumped through the column to pack the particles tightly and to wet them before use. Solid $AgNO_3$ was purchased from VWG International (Espoo, Finland) and symmetrical silica particles of 5 μm diameter were from Waters (Milford, MA, US).

For the extraction, a 25 mm × 25 mm piece was arbitrarily cut from the filter with a special cutter. The square of filter was placed in a vial and the recovery standard was added. Each sample was then sonicated three times in fresh 10 ml *n*-hexane–acetone (1:1 (v/v)) mixture for 30 min. The extracts were filtered through Gelman Acrodisc filters with PTFE membrane and pore size of 0.45 μm (Gelman Sciences, Ann Arbor, MI, US) and concentrated to 100 μl under a gentle stream of nitrogen. The concentrated extract was loaded into the silver impregnated silica column. The non-polar fraction was eluted with 200 μl *n*-heptane and the more polar fraction with 500 μl dichloromethane.

2.3. Equipment

GC × GC–FID experiments were carried out on an Agilent 6890 gas chromatograph equipped with a Hewlett-Packard 7683 split/splitless injector and a flame ionisation detector (FID). Introduction of analytes to the GC column was performed in splitless mode at 300 °C with injection volume of 2 μl. The FID was operated at 300 °C and flow rates for hydrogen, air and nitrogen were 40, 450 and 50 ml/min, respectively. A 1 m × 0.53 mm i.d. diphenyltetramethyldisilazane (DPTMDS) deactivated retention gap from Agilent Technologies (Palo Alto, CA, US) was connected to a 20 m × 0.25 mm i.d. 5% phenyldimethylpolysiloxane column with 0.25 um film thickness (ZB-5, Phenomenex, Torrance, CA, US). The end of the first column was further connected to a 1 m × 0.1 mm i.d. 14% cyanopropyldiphenylmethylpolysiloxane column with 0.1 μm film thickness (BGB-1701, BGB-Analytik, Zürich, Switzerland). Columns were connected to each other by specially made low-volume pressfit connectors purchased from BGB Analytik. Helium (Oy Aga Ab, Espoo, Fnland, purity 99.996%) in constant flow mode was used as carrier gas with head pressure of 170 kPa at 60 °C. The GC oven was temperature programmed as follows: 60 (6 min) then 5°/min to 280 °C, and, finally, 1°/min to 290 °C. Modulation was performed with a laboratory made semi-rotating cryogenic modulator [30] with modulation time of 5 s.

An Agilent 6890N gas chromatograph equipped with a Hewlett-Packard 7683 on-column injector and HP 5973 mass selective detector was used in the GC × GC–QMS experiments. The columns were as follows: retention gap 3 m × 0.53 mm i.d. (deactivated with DPTMDS), first column 30 m × 0.25 mm × 0.25 μm (HP-5MS) and second column 1.2 m × 0.1 mm × 0.1 μm thickness (BGB-1701). The interface between the GC and the MS was maintained at 290 °C, and the ionisation source at 230 °C. Ionisation was done by electron impact ionisation at 70 eV. Ions from 75 to 280 were monitored with a scanning rate of 18.94 scans/s. Modulation was performed with the same modulator as in the GC × GC–FID experiments. Also the chromatographic conditions (temperature program and carrier gas head pressure) were the same as for the GC × GC–FID.

Raw signals acquired by an HP Chemstation were exported in ASCII format. The generation of contour plots and the peak integration were done with a laboratory-written Matlab (The MathWorks, Natick, US) script.

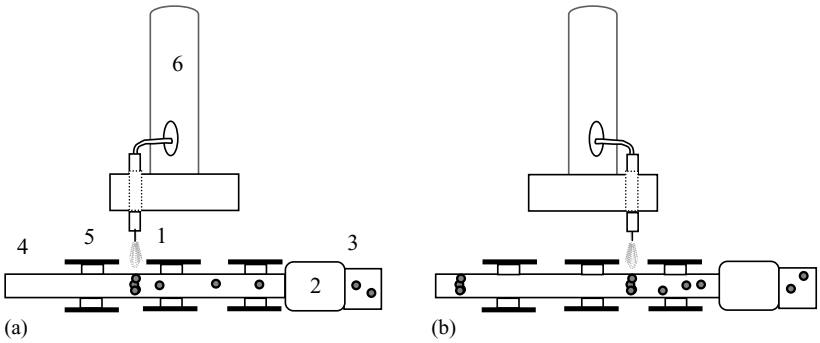

Fig. 1. Schematic drawing of the semi-rotating cryogenic modulator: (a) position 2; (b) position 1. (1) Nozzle spraying CO_2; (2) press-fit connector; (3) first column; (4) second column; (5) column holder plate and septa; (6) rotating shaft.

3. Results and discussion

3.1. Modulation

Modulation was performed with a laboratory-made semi-rotating cryogenic modulator (Fig. 1). Modulation was based on two-step cryogenic trapping using liquid carbon dioxide. The carbon dioxide is sprayed onto the column through a nozzle above the column. When the nozzle rotates 180° from position 2 to position 1, the collected fraction is desorbed by heated oven air and introduced to the second column (Fig. 1a and b). During the injection the CO_2 spray in position 1 prevents the unmodulated analytes from drifting into the second column (Fig. 1b). The total modulation time consists of the two steps, the duration of which can be varied. In this study, the duration of the first step (position 1) was 3 s and that of the second step (position 2) 2 s. The total modulation time was thus 5 s.

The repeatability of the retention times was good along both axes considering both absolute and relative retention times. The average relative standard deviations (R.S.D.) for absolute retention times in the first and second columns were 0.1 and 2.7%, respectively. Relative retention times were obtained by dividing the retention time of the analyte by the retention time of the quantification standard. The corresponding relative values were 0.1 and 2.8%, for the first and second columns, respectively. Further details of the modulator and its performance are given in Ref. [30].

3.2. Sample cleanup

When the combination of a non-polar and a semi-polar column is used in GC × GC, compounds with similar boiling points will be overlapped after the first column separation. If the compounds differ in polarity they will be separated in the second column. Thus, semi-polar PAHs in aerosol particles will be separated from the non-polar saturated hydrocarbons. Unfortunately, the concentrations of the aliphatic hydrocarbons are much higher than those of the aromatic hydrocarbons [31,32], which mean that without clean-up or fractionation, the second column would easily be overloaded by the large amount of hydrocarbons, with serious distortion of the peaks. The target analytes would then easily emerge in the tail of the intense hydrocarbon peak. Although analytes would be identifiable, the quantitative analysis could suffer. Besides reducing the problem of peak distortion, the clean-up procedure also improves the sensitivity of the method because a larger amount of sample can be injected to the GC without the risk of overloading. For these reasons, clean-up was carried out as part of the sample preparation.

The clean-up procedure was optimised with a standard solution containing *n*-alkanes, PAHs and oxy-PAHs. The volume of the solution loaded to the column was optimised to prevent overload and breakthrough of the analytes. Sample volumes from 100 to 300 μl were tested, and elution of *n*-alkanes from the column was found to begin when the volume exceeded 100 μl. The amount of solvent needed for

the elution of the target compounds was thus further examined with a solvent volume of 100 μl. *n*-Heptane was used to elute the *n*-alkanes and dichloromethane (DCM) to elute the PAHs and oxy-PAHs. When too large a volume of *n*-heptane was employed, the low molecular weight PAHs appeared in the *n*-alkane fraction. 200 μl of *n*-heptane was found to be enough to elute the non-polar components while the volume of DCM for the more polar compounds was optimised at 500 μl.

The recovery of the *n*-alkanes was good with the mean value of 93%. The recoveries in the DCM fraction varied with the molecular weight of the components: the higher the molecular weight, the better the recovery. The average value was 67%. In case of real samples, the low molecular weight PAH components may easily be lost during sample preparation if evaporation of the solvent is employed. In addition, it has been noted that, in the atmosphere gas-particle partition is strongly dependent on molecular weight [33] and the low molecular weight PAHs tend to be in gas phase rather than in particulate phase. PAHs even up to fluoranthene and pyrene (MW = 202) have been shown to exist also in gas as well as in particulate phase [33]. Also sampling artefacts, including adsorption of gaseous species [34], mean that reliable results are not necessarily achieved for low molecular weight components. The lowest molecular weight PAHs were therefore excluded from the study. The recovery correction was made to final results (see Section 3.5).

3.3. Calibration

Usually, peak areas or heights are used for determining the concentration dependence. In GC × GC a single component is divided into several fractions, and the individual peaks for a component must be integrated using conventional integration algorithms and then the total area or height for the compound is obtained by summation. This manner has successfully been used by several groups [35,36]. Without an automated program, the summing is a laborious procedure. GC × GC provides a three dimensional signal in which *x*- and *y*-axis represent the retention times and *z*-axis represents the detector response, and concentration can be expressed as volume. In our earlier work [24], we showed that peak volumes can be used equally as well as areas for the calibration. We also found that, in case of three-dimensional signal, the peak volumes provide more repeatable results than the peak heights. Thus, the peak volumes were chosen for quantification.

Contour plots were generated with a Matlab-written script, and a peak to be integrated was indicated by a square on the contour plot. Peaks were marked manually, but there is also an option for automated peak finding. The ratio of the volume of the analyte peak to the volume of the quantification standard was plotted as a function of the ratio of the amount of analyte to the amount of quantification standard. The calibration consisted of seven points with three replicates at each point. The linearity of the calibration curves was good from 0.025 to 2.5 pg/μl, with R^2 values of at least 0.994 for all compounds. The calibration range corresponds atmospheric concentrations from 0.18 to 18 ng/m^3. The repeatability of the peak volumes varied between 4.4 and 8.2% for the whole calibration series. Limits of detection (LOD) and quantification (LOQ) were calculated as the concentration that would give a peak equal to 3 and 10 times the baseline noise, respectively. The estimated LOD was 0.18 ng/m^3 and the LOQ 0.27 ng/m^3.

Some components, for example phenanthrene and anthracene, were quantified together owing to their close elution along the first dimension axis. The limitation was due to the limited number of data points along that axis. The modulation started at 10.00 min and ended at 60.00 min. The 50 min modulation with data acquisition rate of 100 Hz produced about 300,000 data points. When the raw signal was sliced and plotted as a contour plot the data points were divided so that on the first dimension axis there was one data point on every 5 s. The number of data points along the second axis was much larger, roughly 500 points for 5 s. The size of the data point matrix was 600 (1st dimension) × 502 (2nd dimension). One way to increase the peak width along the first axis is to slow the separation, for example by decreasing the temperature program rate. However, this would result in long analysis times, which we wish to avoid. Another option is to increase the sampling rate, in the manner that Prazen et al. [37] did when they applied a chemometrical approach in the quantification of volatile organic compounds. This, on the other hand, requires a special data collection system.

Table 1
Compounds tentatively identified in urban aerosols by GC × GC–FID

Compound	Standard		Sample	
	First RT (min)	Second RT (s)	First RT (min)	Second RT (s)
Phenanthrene/anthracene	33.48	2.67	33.46	2.60
Fluoranthene	38.95	2.86	38.94	2.88
Pyrene	39.94	2.88	39.94	2.94
Benzo(a)anthracene/chrysene	45.65	3.07	45.76	3.07
Benzo(k)fluoranthene	50.30	3.29	50.29	3.28
Benzo(a)pyrene	51.50	3.43	51.54	3.43
Indeno(1,2,3-cd)pyrene/dibenzo(ah)anthracene	56.67	5.11	56.69	5.02
Benzo(ghi)perylene	58.05	5.59	58.05	5.54
9H-fluorenone	32.55	2.96	32.52	2.85[a]
9,10-anthracenedione	37.28	3.04	37.25	3.00
7H-benz(de)anthracen-7-one	46.29	3.40	46.28	3.41
5,12-Naphthacenedione	48.96	3.39	48.95	3.38

The first and second dimension retention times (RT) for standards and samples are shown.
[a] Retention time deviation in the second dimension greater than 2.7% of that of standard (see Section 3.4 for further details).

3.4. Identification

The target compounds were identified in two steps. First, a sample with spiked standards was analysed by GC × GC–FID and the retention times of the analytes in the standards and samples were compared. Secondly, GC × GC–QMS separation was applied.

Compounds tentatively identified by GC × GC–FID are listed in Table 1. As can be seen, correlation between the retention times of the standards and samples is good. Only 9H-fluorenone showed a slight deviation. The allowable variation in retention time for the second column was calculated from the retention time of the analyte in the standard and the average R.D.S. value of 2.7% (see Section 3.1). The second column retention times of 9H-fluorenone exceeded the range when the standard and the sample were compared. The probable reason for the deviation is wrong identification. The tentative identification was checked by GC × GC–QMS with special attention to 9H-fluorenone.

Mass spectrometric detection is favoured when the reliable identification of target compounds or screening for unknowns is of interest. Because of the requirements for high sampling rate in GC × GC, a time-of-flight mass spectrometer (TOFMS), which has scanning capability of more than 50 scans per second [38,39], is usually recommended. However, the GC × GC system coupled to a quadrupole mass spectrometer (QMS) has also successfully been applied by Frysinger and Gaines [40]. They used total ion monitoring with a scanning rate of 2.34 scans/s. The data acquisition rate of the QMS can be increased by narrowing the monitored mass range and by decreasing the number of measurements done with each mass or by using selected ion monitoring when only masses of the target compounds are monitored. Selected ion monitoring provides increased sensitivity but does not allow the identification of unknowns. Encouraging results obtained by GC × GC–QMS with narrow monitored mass range were recently presented [41].

Molecular masses of the target analytes varied between 178 and 278, and to include also the fragments of these compounds, the mass range from 75 to 280 amu was monitored. This provided 18.94 scans/s, which is not fast enough for quantitative analysis but quite suitable for qualitative screening. The length of the second column was increased from 1 m used with the FID detection to 1.2 m in order to diminish the effect of the vacuum in the GC × GC–QMS on the retention of analytes. Otherwise the chromatographic conditions were the same as in GC × GC–FID. Despite of almost similar systems the retention times of GC × GC–FID and GC × GC–QMS chromatograms were not exactly the same. As can be seen in close-up views (Fig. 2a and c) retention of analytes along the first column axis is about 2 min faster in the GC × GC–QMS than in GC × GC–FID experiments. Lower

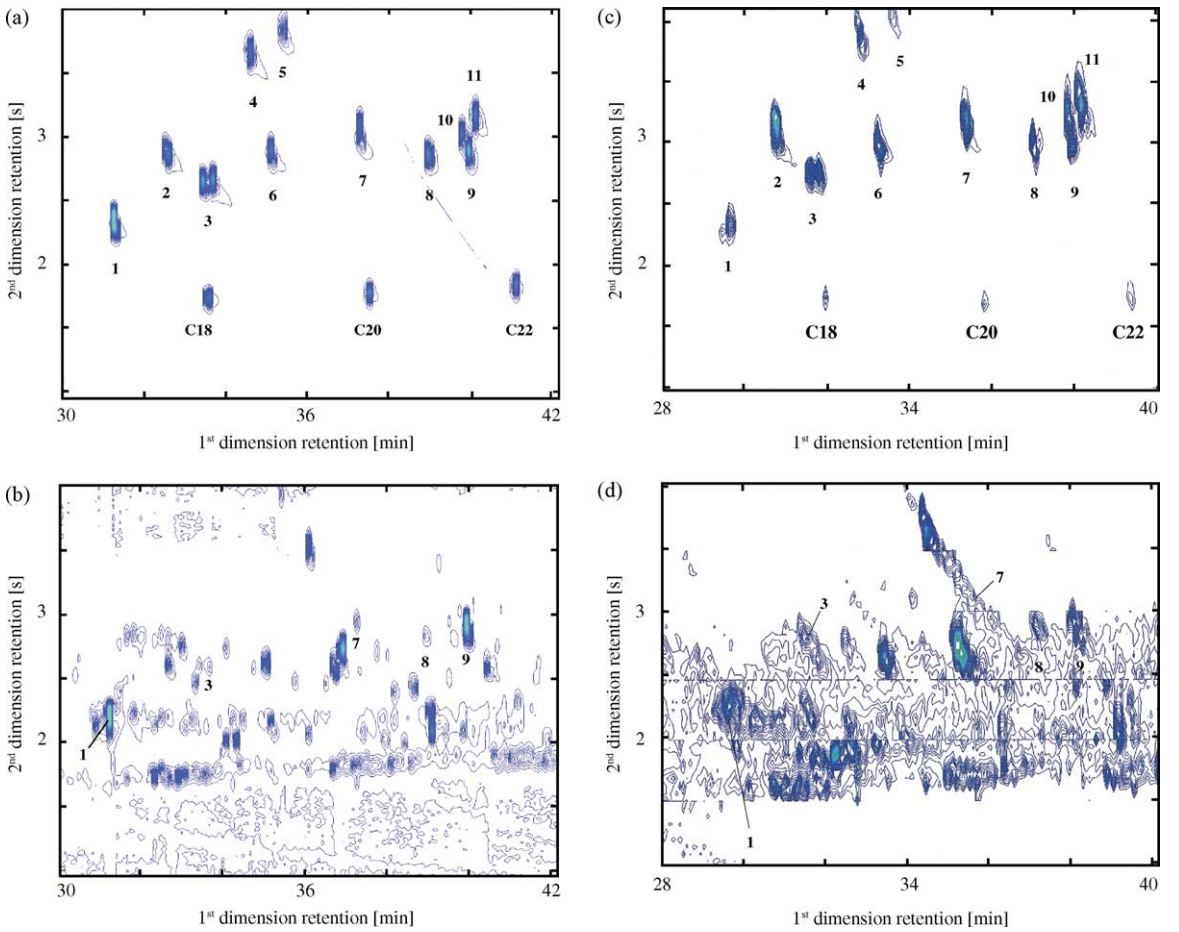

Fig. 2. Contour plot close-up views of standards (a and c) and samples (b and c) obtained by GC × GC–FID and GC × GC–QMS (TIC). Identification: (1) 4,4-dibromaoctafluorobiphenyl; (2) 9H-fluorenone; (3) phenanthrene/anthracene; (4) carbazole; (5) acenaphthenequinone; (6) xanthone; (7) 9,10-anthracenedione; (8) fluoranthene; (9) pyrene; (10) 2-methylnaphthacequinone; (11) phenanthrene-9-carboxaldehyde.

first dimension column elution temperature in GC × GC–QMS resulted in slightly increased second dimension retention times. However, fully aligned retention times between GC × GC–FID and GC × GC–QMS was not the main aim of the study. In order to identify the target compounds the mass-to-charge ratios of interest were extracted from the total ion chromatogram.

The final analysis by GC × GC–QMS confirmed the tentative identifications obtained by GC × GC–FID (Table 2) for most of the target analytes. In the beginning only 9H-fluorenone was suspected to be wrongly identified with standard addition method because of the deviation in the retention times. The suspicion was proved to be right with GC × GC–QMS: 9H-fluorenone was not found in aerosol samples. However, in cases of dibenzo(ah)anthracene and 5,12-naphthacenedione not even matching retention times guaranteed right identification when only standard addition method was used. These compounds were neither found by GC × GC–QMS. Finally, benzo(ghi)perylene was not found by GC × GC–QMS but was found normal GC–MS (i.e. without modulation) and unlike the others it was included in the results. Probably this compound was not found by GC × GC because of the insufficient scanning rate for narrow GC × GC peaks, which decreased the sensitivity. Close-up views of GC × GC–FID and GC × GC–QMS separations with standard solution and sample are shown in Fig. 2a–d.

Table 2
The identified and quantified target analytes and preliminary identified non-target analytes (see Section 3.4 for further details) in urban aerosols

	Molecular weight	Concentration (ng/m^3)
Target analytes		
Phenanthrene/anthracene	178	0.77 ± 0.06
Fluoranthene	202	0.63 ± 0.07
Pyrene	202	>5.48 ± 1.38[a]
Benzo(a)anthracene/chrysene	228	1.28 ± 0.05
Benzo(k)fluoranthene	252	1.16 ± 0.11
Benzo(a)pyrene	252	0.49 ± 0.12
Indeno(1,2,3-cd)pyrene	276	0.67 ± 0.09
Benzo(ghi)perylene[b]	276	0.50 ± 0.07
9,10-Anthracenedione	208	0.64 ± 0.16
7H-benz(de)anthracen-7-one	230	0.96 ± 0.33
Non-target analytes		
Trimethylnaphthalene	170	
Methylfluorene	180	
Methylanthracene/phenanthrene	192	
4H-cyclopenta(def)phenanthrene	192	
Methylpyrene	216	
11H-benzo(b)fluorene	216	
Cyclopenta(cd)pyrene	226	
Benzo(ghi)fluoranthene	226	
C4-phenanthrene/anthracene	234	
Methylchrysene	242	
9-Phenylanthracene	254	
Phenylmethylene-9H-fluorene	254	
Dimethylanthracenedione	236	

Compound name, molecular weight and concentration (mean ± standard deviation; $n = 4$) are shown.
[a] Not extracted completely (see Section 3.5 for further details).
[b] Identified by GC–MS (see Section 3.4).

To briefly test the automated library search option of the mass spectrometer software, a modulated GC × CC–QMS chromatogram from 30 to 60 min was search for other polycyclic aromatic compounds. Altogether approximately 1500 peaks were found, and some of the PAHs are shown in Table 2. The quality values were not good for most of them owing to the rather slow sampling rate of MS and the limited mass range, but the search provisionally indicated the presence of substituted PAHs.

3.5. Concentrations of particulate PAHs and oxy-PAHs

At the time of the sampling in February 2003, the 24-h average temperature was −0.5 °C. Wind direction was westerly but turned to northerly at the end of the sampling. This means that air masses came from the mainland, not from the sea. No precipitation occurred during the sampling.

The recovery corrected concentrations of the quantified components are listed in Table 2. The PAH concentrations ranged from 0.5 to 5.5 ng/m^3. The results are of the same order of magnitude as the results reported from other parts of Europe during winter. Harrison et al. [8] have reported that concentrations of particulate PAHs in February in Birmingham, UK, varied between 0.39 and 2.36 ng/m^3. Kiss et al. [12] have reported winter concentrations of PAHs in Hungary ranging from 0.036 to 5 ng/m^3. Nielsen et al. [42] measured concentrations of 0.6–9.3 ng/m^3 at a busy street and concentrations of 0.18–2.9 ng/m^3 in a city park in Copenhagen, Denmark. In addition to PAHs two oxy-PAHs were quantified (Table 2) and the concentrations were 0.6 ng/m^3 for 9,10-anthracenedione and 1.0 ng/m^3 for 7H-benz(de)anthrace-7-one being on the same level as in other studies. Schnelle-Kreis et al. [43] report oxy-PAHs in Munich, Germany ranging from 0.16 to 3.1 ng/m^3; Allen et al. [7] reports values of 0.041–1.766 ng/m^3 for Boston, US and König et al. [44] values of 0.05–2.05 ng/m^3 for Duisburg, Germany.

The concentration of pyrene was high compared with the concentrations of other compounds. When two samples were extracted with an additional volume of 3× 10 ml hexane-acetone mixture, pyrene was the only compound found in the extracts. The reason for such a large amount remains unclear. Monthly average concentrations of PAHs for February measured at the railway station in downtown Helsinki have been reported [15]. The concentrations of phenanthrene, fluoranthene and pyrene were 0.06, 0.23 and 0.27 ng/m^3, respectively, which are much lower than the concentrations obtained here. However, concentrations of benzo(a)pyrene and benzo(ghi)perylene were 0.56 and 0.41 ng/m^3, respectively, which are quite in line with the results of the present study. It has been suggested that pyrene, along with fluoranthene and phenanthrene are markers of incineration [8]. Thus, a probable explanation for the present of high pyrene concentration is a local incineration source. In addition, high pyrene and fluoranthene concentrations have been reported in exhaust of diesel-powered heavy-duty trucks [45,46]. Exact determination of the source is difficult.

4. Conclusions

The GC × GC method developed performed well in the analysis of aerosol particulates. Sample preparation increased the reliability and sensitivity. The results obtained by GC × GC–FID and GC × GC–QMS were in general agreement but showed that MS detection is required for reliable identification. Several polycyclic aromatic hydrocarbons and oxygenated polycyclic aromatic hydrocarbons were identified and quantified in aerosol particulate samples collected in urban Helsinki.

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