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Determination of organic compounds from wood combustion aerosol nanoparticles by different gas chromatographic systems and by aerosol mass spectrometry

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ABSTRACT

Organic compounds in atmospheric nanoparticles have an effect on human health and the climate. The determination of these particles is challenged by the difficulty of sampling, the complexity of sample composition, and the trace-level concentrations of the compounds. Meeting the challenge requires the development of sophisticated sampling systems for size-resolved particles and the optimization of sensitive, accurate and simple analytical techniques and methods. A new sampling system is proposed where particles are charged with a bipolar charger and size-segregated with a differential mobility analyzer. This system was successfully used to sample particles from wood pyrolysis with particle sizes 30–100 nm. Particles were analyzed by four techniques: comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry, gas chromatography–time-of-flight mass spectrometry, gas chromatography–quadrupole mass spectrometry, and aerosol mass spectrometry (aerosol MS). In the chromatographic techniques, particles were collected on a filter and analyzed off-line after sample preparation, whereas in the aerosol MS, particle analysis was performed directly from the particle source. Target compounds of the samples were polyaromatic hydrocarbons and n-alkanes. The analytical techniques were compared and their advantages and disadvantages were evaluated. The sampling system operated well and target compounds were identified in low concentrations.

1. Introduction

Atmospheric aerosol particles comprise a complex mixture of volatile and semivolatile inorganic and organic compounds. The determination of organic compounds in aerosol particles is of great current interest owing to the potential effects of these compounds on human health and the climate. Although sophisticated analytical techniques are now available, the determination of aerosol composition remains a challenging task owing to the complexity of atmospheric aerosol particles, the difficulty involved in sampling, and the trace-level concentrations of the compounds. Traditionally, aerosol particles have been collected onto filters and the compounds of interest removed by solvent extraction or thermal desorption. Usually, a mixture of particles below a given filter pore size (e.g., $PM_{2.5}$, PM_{10}) has been collected and analyzed. One of the main analytical techniques for this kind of analysis has been gas chromatography followed by mass spectrometry (GC–MS) [1–5]. Owing to the broad variety of compounds present in the samples, a single chromatographic step may fail to separate the components of the mixture, and chromatograms will suffer from severe peak overlap. Such analyses are often preceded therefore, by a fractionation step, in which two or more fractions are separated on a silica or alumina column and analyzed separately [6–11]. Another option to overcome the poor separation efficiency of a single chromatographic column is a multidimensional technique. Comprehensive two-dimensional gas chromatography (GC × GC) has proven to be a powerful technique for air and aerosol analysis [12–14]. Thermal desorption combined with GC × GC and time-of-flight mass spectrometry (TOFMS) [15–17] has also been used satisfactorily. *In situ* analyses have been performed with a lab-made sampling system, followed by thermal desorption and GC × GC [17–19], and solvent extraction followed by GC × GC with TOFMS or a flame ionization detector (FID) has been applied to the determination of organic species in urban [20] and rural aerosols [21].

The smallest fractions of aerosol particles (particles below 100 nm) are receiving special attention because of their potential

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to affect both human health and cloud formation. Unfortunately analyzing the organic fraction of the smallest aerosol particles is challenging owing to the tiny mass and short lifetime of the particles. The particles are readily transported over long distances and can reach deep into living tissue [8,22]. There is growing evidence, moreover that smaller particles are more reactive than larger ones. As noted above, many of the studies addressing the organic composition of aerosol particles deal with a mixture of particle sizes collected onto a single filter. However, only few studies have been carried out where nanoparticles of specific sizes been collected and analyzed to determine specific organic compounds. Ochiai et al. [23] analyzed size-resolved particles, including the nanoparticle fraction with a diameter of 29–58 nm, in roadside atmospheric samples. The samples were collected with a low-pressure impactor, and PAHs were determined by TD–GC × GC–QMS. TD–GC–MS has also been used to determine n-alkanes in atmospheric nanoparticles (29–58 nm) [24] and to determine PAHs in size-segregated particles (120–330 nm) from residential wood combustion [25]. Various aerosol mass spectrometer set-ups have successfully been applied for the analysis of size-segregated organic aerosol particles. Although aerosol mass spectrometry methods are usually non-separative, they are also suitable for *in situ* analysis [26,27].

In this work, we tested the applicability of a particle size-segregation system in which particles are charged with a bipolar charger and size-separated with a differential mobility analyzer (DMA). For GC analysis, the particles were collected on a cellulose filter. The system was used to collect nanoparticles (30–100 nm) generated in wood combustion. Four analytical techniques were compared for the determination of PAHs and n-alkanes in the particles: GC × GC–TOFMS, 1D GC–TOFMS, 1D GC–QMS, and a non-separative aerosol MS technique. Following this, PAHs and n-alkanes were analyzed in a selected aerosol samples by the two best chromatographic techniques and by aerosol MS.

2. Materials and methods

2.1. Chemicals and standard solutions

Acetone and n-hexane (HPLC grade) were purchased from Lab Scan Analytical Sciences (Dublin, Ireland). A standard solution of n-alkanes (even members C10–C40, 100 μg/mL, CERTAN) was purchased from LGC Promochem GmbH (Wesel, Germany). The PAH mixture (naphthalene (1), acenaphthylene (2), acenaphthene (3), fluorine (4), phenanthrene (5), anthracene (6), carbazole (7), fluoranthene (8), pyrene (9), benz(a)anthracene (10), chrysene (11), benzo(b)fluoranthene (12), benzo(k)fluoranthene (13), benzo(a)pyrene (14), indeno[1,2,3-cd]pyrene (15), benzo [ghi]perylene (16), dibenzo[ah]anthracene (17)), containing 2.0 mg/mL of each compound (Z-014G-R) was from AccuStandard (New Haven, USA). Two internal standards were used for the chromatographic analysis: 4,4′-dibromooctafluorobiphenyl (quantification standard, 99%, Sigma–Aldrich, Gillingham, UK) and 1,1′-binaphthyl (98%, internal standard, Across Organics, New Jersey, USA).

2.2. Sampling system

The sampling system (Fig. 1) was set-up in a lab fume cupboard. Aerosol particles were produced by heating a piece of Scotts pinewood with a butane/propane flame. The particles were charged with a bipolar charger and size-separated with a differential mobility analyzer (ratio to aerosol flow to sheath air flow 2:5). In the case of chromatographic analysis the particle sizes of interest were 30–100 nm in diameter, and sampling times were 15–150 min. In the case of aerosol MS the particle sizes were from 30 nm to 90 nm

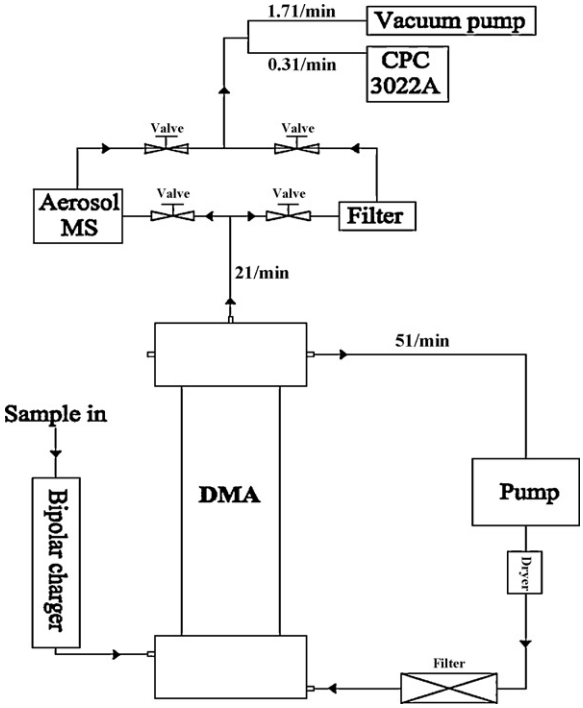

Fig. 1. Aerosol particle sampling system used in the study of particle emission from wood pyrolysis.

and sampling times between 5 min and 30 min. A condensation particle counter (CPC) (3022 A, TSI, MN, USA) was used to count the particles entering the sample syringe filter (0.45 μm, regenerated cellulose, i.d. 15 mm, Phenomenex, CA, USA) or directly passing to the aerosol MS.

2.3. Sample preparation for chromatographic techniques

Aerosol samples were extracted from the filters with 1 ml of hexane/acetone (50/50, v/v%) mixture. Then, 10 μl of 1,1-binaphthyl stock solution (500 mg/L) was added, and sample volume was reduced to 100 μl under a gentle stream of nitrogen. Finally, 10 μl of the quantification standard solution (50 mg/L 4,4′-dibromooctafluorobiphenyl) was added to the samples. Each sample was analyzed three times. A blank sample, obtained by extracting a clean filter with 1 mL of the hexane/acetone (50/50%) mixture and pre-treated as a real sample, was analyzed before each sample.

2.4. Analytical instrumentation and methods

2.4.1. GC–TOFMS and GC × GC–TOFMS

GC–TOFMS and GC × GC–TOFMS experiments were carried out on an Agilent 7890A gas chromatograph (Santa Clara, USA) equipped with a split/splitless injector and interfaced with a LECO Pegasus® 4D TOFMS system (LECO, St. Joseph, MI, USA). The Agilent GC was equipped with a secondary oven and a dual-stage thermal modulator. An HP-5 column (29 m × 0.25 mm i.d., 0.25 μm film thickness) was used as the first-dimension column and an RTX-17 column (79 cm × 0.1 mm i.d., 0.1 μm film thickness) as the second-dimension column (housed in the secondary oven). The two columns were connected by a Silket® Treated Universal Press-Tight® connector (20480) (Restek, Bellefonte, PA, USA). A 2 m × 0.53 mm i.d. DPTMDS deactivated retention gap was connected to the first-dimension column to protect it from deterioration.

The analytical conditions for the GC–TOFMS and GC × GC–TOFMS were identical except for the modulator, which

was turned off for 1D GC analysis. 1 μl sample was introduced by splitless injection (injector temperature 250 °C), and helium was used as carrier gas in constant flow mode (1.00 ml/min). The temperature of the first-dimension column was programmed from 50 °C (5 min) to 260 °C (15 min) at a rate of 5 °C/min and that of the second-dimension column from 70 °C (5 min) to 280 °C (15 min) at a rate of 5 °C/min. The total GC run-time was 62 min. The time needed to achieve the initial conditions after the analysis was 11 min. The transfer line between the second-dimension column and the (TOFMS) was maintained at 280 °C and the ionization source at 200 °C. Electron impact ionization (70 eV) was used, and a mass range of 50–500 amu was recorded with an acquisition rate of 50 Hz.

For GC × GC analysis, the main parameters of the cryogenic modulator were programmed as follows: the modulator temperature offset, relative to the main GC oven, was 30 °C and the optimum modulation time was 5 s, with a 1.90-s hot pulse time and a 0.60-s cooling time between stages. Cooling was done with pressurized gaseous nitrogen cooled by liquid nitrogen using a Euro-Cyl 120/4 portable liquid cylinder to store and dispense the liquid.

Data acquisition and processing were accomplished with LECO® ChromaTOF™ optimized for the Pegasus® 4D software (version 3.34). The software has a large number of functions, such as auto peak find, peak deconvolution, full spectral library search, peak combination, and automatic integration of all peak areas belonging to the same second-dimension peak. After data processing, the software generates a peak table which displays information about the peaks found. Peak name, mass spectral match factors (similarity, probability and reverse), height, signal-to-noise ratio (S/N), and retention time are some of the headings in the table. In this work, data processing was used to find all peaks with an S/N larger than 3. For purposes of this study, the maximum number of unknown peaks to be found was set at 600, and unique mass was used for area/height calculations. For GC × GC chromatograms, the peak width was set at 0.5 s, and a different data processing method was applied to GC–TOFMS chromatograms in which peak width was set at 3 s (all other parameters were kept identical with those used in the GC × GC data processing method). The NIST EI mass spectrum database was used for the spectral search.

2.4.2. GC–QMS

An Agilent 6890N GC equipped with an on-column injector was used for GC–QMS. The GC column was a DB-5HT (30 m × 0.250 mm × 0.1 μm) coupled with a 3-m deactivated retention gap (i.d. 0.53 mm, Agilent, USA) via a Silket® treated universal press-tight® connector (20480) from Restek (Bellefonte, PA, USA). The GC oven temperature was programmed as follows: initial temperature 50 °C (2 min), temperature gradient 10 °C/min and final temperature 380 °C (1 min). The sample (1 μL) was introduced by on-column injection. The injector temperature was in oven tracking mode. The GC run-time was 36 min, and the time needed to return to the initial conditions was 11 min. Helium was used as carrier gas, with a constant flow of 0.8 mL/min. The mass spectrometer was a quadrupole instrument (HP 5973) equipped with an inert ion source operating in electron impact mode and using 70 eV ionization energy. The ion source temperature was 150 °C and the interface between the GC and the quadrupole MS was set to 380 °C.

For the optimization of the analytical conditions of the method, detection was done in scan mode. The *m/z* range was 50–500 amu, and the abundance threshold value was set to zero. The compounds were identified by comparison of the experimental spectra with those of the NIST'98 database (NIST/EPA/NIH Mass Spectral Library, version 1.6).

The information obtained in scan mode allowed establishing of 17 SIM groups. The two most abundant ions of each compound (for hydrocarbons masses 43 and 57, and for PAHs molecular ions) were recorded. Each ion was acquired with a dwell time of 10 ms. Data analysis was performed with Enhanced ChemStation, G1701A Ver. D 00.01.27 software from Agilent Technologies.

2.4.3. Aerosol mass spectrometry

The aerosol mass spectrometer set-up has been presented elsewhere [28]. Some improvements of the system have since been made, and the operation of the modified system is briefly described here. The charged and size-separated particle flow was directed to an oppositely charged stainless steel collection surface, which is part of the specially designed sampling valve. The collected sample was introduced to the high vacuum of the mass spectrometer (MS) by rotating the sampling valve and, after the vacuum recovered (about 60 s), the sample was desorbed from the collection surface with an IR-laser, operating at 1064 nm wavelength. The sample desorption produces a gaseous plume of mostly neutral molecules in the vacuum, which expanded rapidly. Immediately after the desorption pulse, the sample molecules in the plume were ionized with one laser shot from an ArF excimer laser operating at wavelength 193 nm. The ions were then diverted to the TOFMS, separated, and detected according to their *m/z* ratios. In our previous aerosol MS set-up [28] we used a self-made TOFMS as analyzer and an oscilloscope for data acquisition, but here the system was upgraded by using a commercial TOFMS (C-TOF, Tofwerk, Thun, Switzerland) and a data acquisition card (Agilent Acqiris DP211, Switzerland). The sampling surface was changed from platinum to stainless steel.

The aerosol MS system required little parameter optimization and no pre-treatment of samples. The only variables affecting the system were collection efficiency, aerosol flow rate, and mass window in the TOFMS. The mass window is the range on the *m/z* axis where the ions are most efficiently detected and it depends on the ion analysis frequency and timing scheme of the mass spectrometer. The range was between about 50 amu and 200 amu and for one data acquisition, depending on the *m/z* ratio. Thus, during at the one data acquisition the system can detect only a limited number of masses. However, the signal can be divided into different parts so that the whole mass range can be analyzed if required. One can measure a sample with several ranges along the *m/z* axis, for example, the first 0–50 amu, second 50–150 amu, and so on.

The system was used here only for compound identification while the quantitative manner of the instrument was only tested and used for comparison with results obtained by other techniques. The same standard mixture (1 mg/L) containing PAHs and n-alkanes, as used for calibration in chromatographic techniques, was used with the aerosol MS. All aerosol samples were collected on the sampling valve collection surface by using +2.5 kV collection voltage. The aerosol flow rate was 2 LPM and the mass window was adjusted and switched between 100 amu and 350 amu.

3. Results and discussion

In this study, three gas chromatographic techniques were developed for the determination of n-alkanes and PAHs in aerosol particles. The techniques were compared with each other and with aerosol MS in terms of sensitivity, sampling time, amount of work required, and repeatability. Analyzes of nanoparticles (30–100 nm) from wood pyrolysis collected via the sampling system were used for the comparison. Particle concentrations in the different particle sizes during the sampling periods varied between about 10^4 and 10^6 particles/cm^3.

3.1. Analytical characteristics of the techniques

The GC and GC × GC techniques were optimized to achieve the best peak resolution in the shortest possible time. The validation

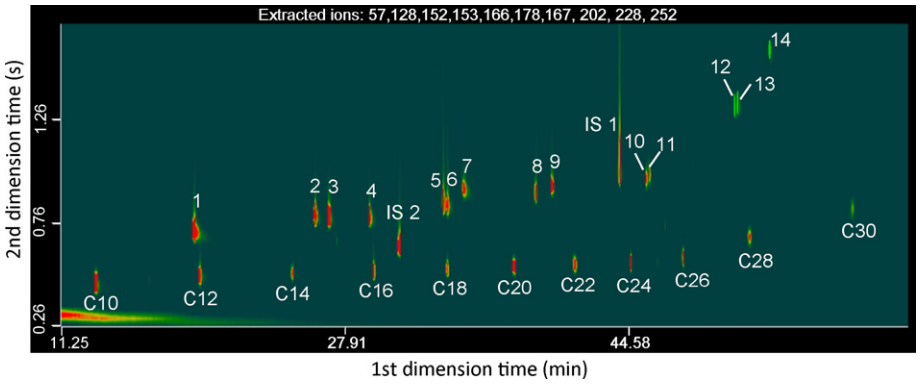

Fig. 2. GC × GC–TOFMS plot of a standard solution of 500 μg/L of PAHs and n-alkanes and 5 mg/L of internal standards 1,1′-binaphthyl and 4,4′-dibromo-octafluorobiphenyl.

parameters, including linearity, repeatability, and limits of detection and quantification, were then determined for each technique. The detection limits (LODs) were calculated as 3.3 times the standard deviation of the peak response for ten replicates ($n = 10$), corresponding to an S/N ratio of about three. The quantitation limits (LOQs) were calculated as LODs using a factor of ten for the deviation [29].

3.1.1. GC × GC–TOFMS

In developing the GC × GC technique, we optimized the modulation frequency and temperature programming to obtain good separation of target analytes. The column combination was chosen on the basis of earlier studies [20]. Fig. 2 shows the optimized separation of the target compounds. As can be seen, all compounds are well separated because of the second column. The peak designations for n-alkanes used in Fig. 2 are based on the number of carbon atoms in hydrocarbon molecule (C10–C28), while the PAHs were numbered according to the numbering in Section 2.1. Because of their high boiling point and thus long analysis time, PAH's 16–18 were excluded from the chromatographic study. The most abundant ion (57 Da) was used for the quantitation of hydrocarbons, while molecular ions were used for PAHs. The separation in the second column was much faster than that in the first (0.84 s *vs.* 57.66 min for triacontane, the target compound with the longest retention time) and was therefore performed under essentially isothermal conditions. Since all the components of an individual fraction are of virtually the same volatility, the separation on the second column depends only on the specific interactions of the compounds with the stationary phase. This two-dimensional separation provides chromatograms in which chemically related compounds show up as ordered structures. The structured chromatograms have been cited as a primary advantage of the GC × GC technique [12,17,20,30–33] and they are highly useful for group-type analyses.

Calibration curves for n-alkanes and PAHs were constructed with the optimized conditions. Seven concentration levels ranging from LOQ to 2000 μg/L were used. Each standard was analyzed in triplicate. Peak areas of the extracted ion chromatograms were used to determine the concentration dependence. The individual second-dimension peaks of each analyte were automatically integrated and summed by the Pegasus® 4D software. Ten compounds were selected for comparison of the analytical characteristics of the methods. Table 1 shows the retention time relative standard deviations (RSD), and limits of detection and quantification. The linearity of the calibration curves was good in the concentration range studied; R^2 values were at least 0.9928 for all compounds. Repeatability, for a concentration level of 500 μg/L, was satisfactory, with an RSD of 7.8% or less.

The detection limits (LODs) were estimated using a 1-μg/L solution for all PAHs except chrysene and benzo(a) pyrene: for these a 5-μg/L solution was needed. Fresh hexane was used for the determination of the baseline deviation under possible n-alkane peaks. The LOD values ranged from 0.2 μg/L to 5.0 μg/L. The quantitation limits (LOQs) ranged from 0.6 μg/L to 24.0 μg/L.

Since the GC × GC–TOFMS detected trace concentrations of some of the n-alkanes in the blank sample and even in fresh hex-

Table 1
Analytical characteristics of different chromatographic techniques for ten selected analytes ($n = 10$).

Compound	Method								
	GC × GC–TOFMS			GC–TOFMS			GC–QMS		
	RSD%[a]	LOD[b] (μg L^{-1})	LOQ[b] (μg L^{-1})	RSD%[a]	LOD[b] (μg L^{-1})	LOQ[b] (μg L^{-1})	RSD%[a]	LOD[b] (μg L^{-1})	LOQ[b] (μg L^{-1})
n-Alkanes									
Dodecane (C10)[c]	4.03	0.2	0.6	2.97	2.7	8.2	1.6	17	52
Hexadecane (C16)	4.88	1.4	4.3	5.03	14.7	44.6	6.6	32	99
Eicosane (C20)	5.00	1.4	4.3	5.64	13.2	40.0	7.2	14	42
Tetracosane (C24)	4.28	3.7	11.3	4.91	14.0	42.5	7.1	32	99
Octacosane (C28)	2.29	7.9	23.9	4.01	21.2	64.4	8.9	49	150
PAHs									
Acenaphthene (3)	1.57	1.1	3.2	4.50	4.8	14.7	4.9	24	72
Phenanthrene (5)	5.42	0.6	1.8	5.96	3.3	9.9	6.1	14	42
Pyrene (9)	4.74	0.5	1.5	6.18	4.7	14.3	5.6	9	26
Chrysene (11)	8.5	1.3	3.9	6.88	6.2	18.9	6.2	23	68
Benzo[a]pyrene (14)	7.78	3.0	9.2	5.54	13.6	41.1	7.7	17	51

[a] Determined at 500 μg L^{-1} level ($n = 10$).
[b] See text Section 3.1.
[c] Designations used for compound identification in chromatograms of Fig. 2.

Fig. 3. Aerosol MS spectra of different particle sizes in samples from wood combustion and standard liquid sample. (A) 30 nm particles collected for 15 min, (B) 50 nm particles collected for 15 min, (C) 70 nm particles collected for 15 min, (D) 70 nm particles collected for 30 min and (E) 1 μl of 10 μg/L standard solution containing PAHs and n-alkanes. The marked ions represent fluoranthene (202), pyrene (202), benz(a)anthracene (228), chrysene (228), benzo(b)fluoranthene (252), benzo(k)fluoranthene (252), benzo(a)pyrene (252), indeno[1,2,3-cd]pyrene (276), benzo [ghi]perylene (276), dibenzo[ah]anthracene (278). Other marked ions were tentatively identified as fragments of high molecular mass alkanes.

ane, the peak areas found in the blanks were subtracted from the peak areas of the standard solutions and the samples.

3.1.2. GC–TOFMS

The column settings and temperature program for the GC–TOFMS separation, were the same as those used in GC × GC–TOFMS. It is clear that the separation of PAHs is not sufficient when compared with the two-dimensional separation. Extracting ion chromatograms will not solve the problem because the molecular ions for the last eluting compounds are the same. We used a relatively simple standard mixture in this research, but in ambient aerosol samples overlapping could be critical.

Table 1 shows the main analytical characteristics of the optimized GC–TOFMS technique. The calibration curves were constructed as described in the GC × GC–TOFMS section. The peak areas from the extracted ion chromatograms were used for quantitation. For the determination of LODs, a 10-μg/L solution was used for all compounds selected except chrysene and benzo(a)pyrene; for these a 50-μg/L solution was used. The R^2 was always above 0.9956; the RSD for a 500-μg/L sample and $n = 10$ was equal to 6.9% or less; the limits of detection ranged between 2.7 μg/L and 21.2 μg/L and the quantitation limits from 8.1 μg/L to 64.3 μg/L.

3.1.3. GC–QMS

The optimized conditions for GC–QMS analysis were similar to those for GC–TOFMS, the main difference was being the faster temperature program. The separation efficiency was not better with slower temperature programming, but the analysis time was increased substantially and so the faster program was used. Five levels ranging from 200 μg/L to 2000 μg/L were used to construct the calibration curves. Each standard solution was analyzed in triplicate. The peak areas for the quantitation ions in the extracted ion chromatograms were used as calibration variables.

The analytical characteristics of the GC–QMS technique are shown in Table 1. A 30-μg/L solution was used for the determination of LODs of the PAHs and n-alkanes. The R^2 values were at least 0.9952 for all compounds. Repeatability, for a concentration level of 500 μg/L and $n = 10$, was satisfactory, with an RSD of 8.9% or less. The limits of detection ranged from 9 μg/L to 49 μg/L and the quantitation limits between 26 μg/L and 150 μg/L.

3.1.4. Aerosol MS

The aerosol MS system showed good sensitivity for the standard PAH and n-alkane solutions. 1 μl of the 10 μg/L standard solution was sufficient to give detectable signals of PAHs 8–17. Higher concentrations (1 mg/L solution) were needed to see the

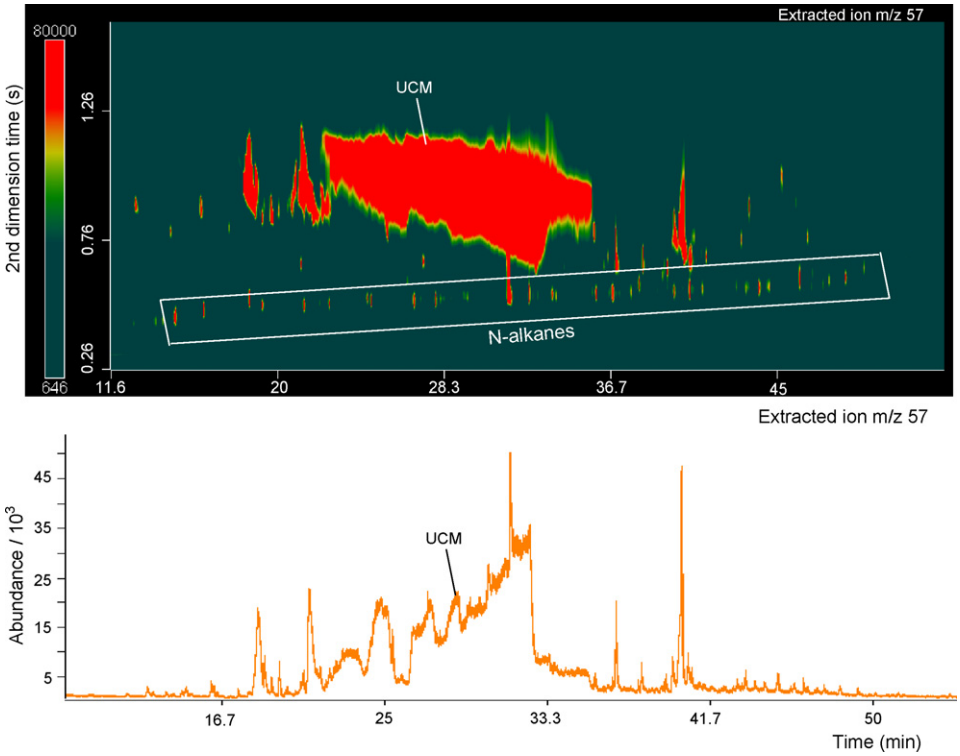

Fig. 4. Comparison of GC × GC–TOFMS (top) and GC–TOFMS (bottom) extracted ion chromatograms of a 100-nm sample collected for 15 min.

alkanes because fragmentation of the n-alkanes makes the individual identifications difficult. When mass window was adjusted to 50–100 amu the alkane pattern (chain loss of 14 amu corresponds to loss of CH_2) could be identified. Unfortunately there was too much variation between the standard samples at every concentration level to allow quantitative analysis. This variation is probably due to the varying cleanliness of the sample collection surface and artifact formation during the laser desorption process. The data acquisition card also had its limitations: signals of greater than 50 mV intensity were recorded as of 50 mV intensity. Many signals at standard samples should have been stronger signals. It is also relevant that aerosol MS produces many different spectra from the same sample. Normally a single sample will produce about 20–30 spectra, which are subsequently added together manually. The sample compounds and desorption laser intensity determine how long the sample is viable. This feature of the aerosol MS will also generate some uncertainties for the instrument's quantitative nature.

The standard aerosol MS spectrum was compared with the average spectrum of the total ion chromatogram (TIC) from GC–MS, and many of the same peaks were seen in the two spectra. These peaks include PAH molecular ions (all those for standard solution except naphthalene) and some alkane peaks (e.g., *m/z* 43, 57, 71 and up to 295). These ionization methods (EI in the chromatographic techniques and photo ionization in aerosol MS) are comparable at least in some degree since the photo ionization produced a similar spectrum with less fragments in the area of small *m/z* values. Occasionally the M^+ ion was seen more easily with photo ionization.

The aerosol MS was sensitive and able to detect target compounds in wood smoke aerosol particles. Particle collection times were generally shorter than in filter collections but signals were still detected, especially for PAH compounds. An example of an aerosol MS spectra is presented in Fig. 3. From this figure, some PAHs and alkanes were identified by comparison with the spectrum of the standard solution. Further, there was some variation in the ions detected in different samples because wood is not uniform material, and nor is burning process ever the same. Considerable differences in the produced aerosol particles can therefore be expected. Particle concentrations were roughly the same in all samples (10^5 particles/cm^3) and since the collection time was kept constant the peak intensities increased with the particle size. (Particle size has a cubic dependence on the particle mass.)

3.2. Comparison of the chromatographic techniques

Comparison of the analytical characteristics of the three optimized chromatographic techniques showed the repeatabilities to be closely similar and the calibration plots for the target compounds to be linear over the range studied (about one order of magnitude). The main difference between the analytical characteristics of the techniques studied is the sensitivity. The most sensitive chromatographic technique was GC × GC–TOFMS, with limits of detection 3–13 times lower than those obtained with GC–TOFMS, and 6–80 times lower than those obtained with GC–QMS.

The GC × GC–TOFMS and GC–TOFMS techniques differed only in a use of the modulator between the two chromatographic columns, which means that the increase in sensitivity achieved with GC × GC must be due to the cryofocusing of the compounds eluted from the first column.

The area obtained upon summing the peaks corresponding to a compound in the extracted ion chromatogram obtained by GC × GC–TOFMS was the same as the peak area obtained on analyzing the same solution by GC–TOFMS. However, the peak width at half-height was about 58 times greater for the peaks obtained by 1D GC. This was reflected as an increase of about 14-fold in the signal-to-noise ratio (S/N) with the GC × GC technique relative to the ratio for 1D GC. As a result, the limits of detection (described above) were significantly lower with the GC × GC technique, in agreement with the findings of others, as recently reviewed [32]. Thus, Lee et al. [34] reported a 4–5-fold sensitivity gain for GC × GC–FID and Dal-

lüge and co-workers [30] calculated a 2–5-fold improvement for GC × GC–TOFMS. Similar results were reported for GC × GC-μECD, with LODs 3–5 times lower than in 1D GC [35].

The increase in sensitivity obtained with using 1D GC–TOFMS relative to 1D GC–QMS is of the order of 1–6-fold. This is probably due to the detector employed, since 1 μL of sample was injected in both cases and the chromatographic columns were similar. The addition of a second column to 1D GC–TOFMS has no effect on the separation in 1D mode. Moreover, the TOFMS was programmed with an acquisition rate of 50 spectra/s (can be increased up to 500), so that a much more precise reconstruction was obtained with TOFMS than with the QMS detector in SIM mode, where about 24 spectra/s were recorded for SIM groups composed of two ions and 16 spectra/s for SIM groups with four ions.

To achieve limits of detection of the same order as those obtained by GC × GC–TOFMS it would be necessary to increase the sampling time of the aerosol particles and simultaneously increase the particle mass at the filter. Sample volume could also be increased.

One drawback of GC × GC relative to 1D GC is that more time is required for analysis. This is because optimal results it require the use of at least three or four modulations over each first-dimension peak, and this limits the temperature ramps used in the main oven, usually in the 0.5–5 °C/min range [12]. We used a ramp of 5 °C/min in the GC × GC–TOFMS analysis and the total time to record the chromatogram was 62 min; the ramp used in the GC–QMS technique was 10 °C/min, affording a GC run-time of 36 min; i.e., a reduction of almost 50%. Additionally, the equipment for 1D GC is less expensive and more common in analytical laboratories. Another drawback consistently associated with the use of GC × GC is that processing of the large data files that are generated is complex and time-consuming. Fortunately, the new Pegasus® 4D software (version 3.34) with its built-in automatic functions simplifies the data treatment substantially. However, manual supervision of an experienced analyst is still required, which makes data treatment more complex than in conventional 1D analysis.

3.3. Comparison of techniques for determining the target compounds in aerosol samples

A 100-nm aerosol sample collected for 15 min was used for comparison of the chromatographic techniques. The compounds were extracted from the filter and the sample was analyzed immediately by the chromatographic techniques. The aerosol MS technique is compared separately since the samples were different from those used in the chromatographic techniques.

First, the collected sample was analyzed by GC × GC–TOFMS. Concentrations were of the same order as the limits of quantitation estimated for the GC–QMS, and even lower for some compounds, and we therefore excluded the GC–QMS technique from this part of the study.

Fig. 4 shows the extracted ion chromatograms for n-alkanes (*m/z* 57) obtained from the 100-nm sample by GC × GC–TOFMS and GC–TOFMS techniques. Both chromatograms show a region, called the unresolved complex mixture (UCM), whose spectrum mainly corresponds to that of levoglucosan (a specific biomarker of biomass combustion). In the chromatogram obtained by GC–TOFMS, it is seen that for the extracted *m/z* ratio, some of the n-alkanes are totally overlapped by the non-resolved interfering matrix constituents, preventing their identification and hence their quantification. An attempt was made to solve this problem by selecting another *m/z* ratio from the spectrum of the n-alkanes. The same overlap was observed for all *m/z* ratios studied, however. Thus, to achieve correct identification and quantification of all the n-alkanes by GC–TOFMS the sample would have to be subjected to a pre-treatment step (e.g., solid-phase extraction) before analysis. Including this pre-treatment step would increase the analysis time and also the associated error, since sample pre-treatment is typically a major source of error in an analytical technique.

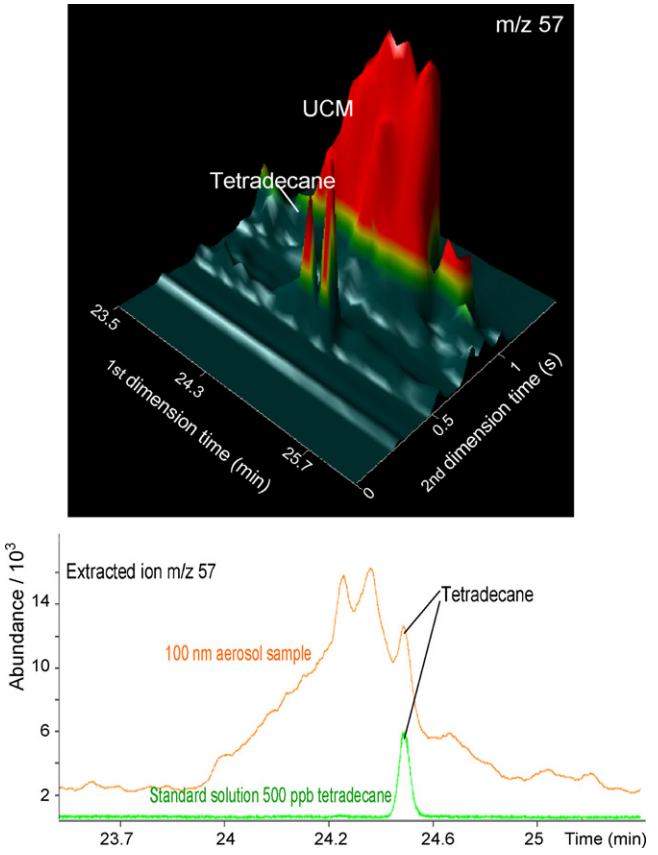

Fig. 5. Comparison of GC × GC–TOFMS (top) and GC–TOFMS (bottom) extracted ion chromatograms of tetradecane in a 100-nm sample.

The two-dimensional chromatogram, obtained by GC × GC–TOFMS, showed a better separation of the analytes from interfering matrix constituents. In this case, the n-alkanes were perfectly separated from the interfering matrix elements and could be identified and quantified without the inclusion of additional steps. As an example, Fig. 5 shows the 3D chromatogram of tetradecane in comparison with that obtained by 1D GC. As can be seen, the comprehensive separation achieved by GC × GC affords a much larger peak capacity, which is highly useful for complex real samples and hence can be considered the main reason for the success of the comprehensive approach. The same result has been widely reported elsewhere [12,17,31,32].

Table 2 shows the concentrations of the target compounds found in the 100-nm sample by the GC–TOFMS and GC × GC–TOFMS techniques. The confidence interval is expressed for three replicates with a confidence level of 95%. The portion of the calibration curve of a compound that provides the lowest confidence interval was selected for determining the concentration of that compound in samples.

There was some variation in the compounds detected in the filter samples of different particle size (Tables 3 and 4). In general concentrations were at the same level for the n-alkanes but differed widely for the PAHs. The PAH concentrations were highest in the 50-nm particle samples and the lowest in the smallest particles (30 nm). Concentrations of heavier n-alkanes (<C12) increased as the particle size increased from 30 nm to 70 nm. In the 100-nm sample, however, alkane concentrations were generally lower than in 70-nm samples. Repeated injections of a single

Table 2
Concentrations of the target compounds found in a 100-nm aerosol sample analyzed by GC × GC–TOFMS and GC–TOFMS.

Compounds	Concentration (μg/L)	
	GC × GC–TOFMS	GC–TOFMS
n-Alkanes		
Decane	35 ± 5	20 ± 10
Dodecane	48 ± 2	60 ± 8
Tetradecane	160 ± 20	150 ± 2
Hexadecane	150 ± 10	130 ± 10
Octadecane	280 ± 20	–
Eicosane	260 ± 20	–
Docosane	320 ± 20	–
Tetracosane	310 ± 20	–
Hexacosane	400 ± 20	–
Octacosane	180 ± 30	150 ± 20
Triacontane	200 ± 30	170 ± 30
PAHs		
Naphthalene	18 ± 6	18 ± 6
Acenaphthylene	17 ± 4	11 ± 5
Acenaphthene	7 ± 4	<LOQ
Fluorene	11 ± 5	<LOQ
Phenanthrene	120 ± 10	100 ± 10
Anthracene	26 ± 4	33 ± 9
Carbazole	9 ± 4	7 ± 3
Fluoranthene	350 ± 20	300 ± 10
Pyrene	360 ± 20	300 ± 10
Benz(a)anthracene	100 ± 20	90 ± 20
Chrysene	60 ± 10	90 ± 30
Benzo(b)fluoranthene	70 ± 20	80 ± 30
Benzo(k)fluoranthene	52 ± 6	50 ± 10
Benzo(a)pyrene	70 ± 10	40 ± 7

Compound overlapped with matrix.
LOQ = Limit of quantitation.

Table 3
Concentration of the target compounds in samples of different particle sizes analyzed by GC × GC–TOFMS.

Compounds	Concentration in different size samples (μg/L)			
	30 nm	50 nm	70 nm	100 nm
n-Alkanes				
Decane	24 ± 5	26 ± 5	41 ± 5	35 ± 5
Dodecane	31 ± 2	40 ± 2	49 ± 2	48 ± 2
Tetradecane	80 ± 10	120 ± 10	190 ± 10	160 ± 20
Hexadecane	40 ± 10	50 ± 10	160 ± 10	150 ± 10
Octadecane	100 ± 20	82 ± 20	300 ± 30	280 ± 20
Eicosane	70 ± 10	120 ± 10	350 ± 20	260 ± 20
Docosane	130 ± 10	180 ± 20	460 ± 20	320 ± 20
Tetracosane	150 ± 10	200 ± 10	600 ± 20	310 ± 20
Hexacosane	200 ± 10	230 ± 20	890 ± 90	400 ± 20
Octacosane	140 ± 30	120 ± 20	550 ± 40	180 ± 30
Triacontane	150 ± 30	140 ± 30	480 ± 50	200 ± 30
PAHs				
Naphthalene	11 ± 6	15 ± 6	20 ± 6	18 ± 6
Acenaphthylene	10 ± 4	79 ± 4	19 ± 4	17 ± 4
Acenaphthene	<LOQ	17 ± 4	11 ± 4	7 ± 4
Fluorene	11 ± 5	33 ± 4	19 ± 4	11 ± 5
Phenanthrene	37 ± 6	320 ± 10	52 ± 6	120 ± 10
Anthracene	11 ± 4	63 ± 3	22 ± 4	26 ± 4
Carbazole	<LOQ	<LOQ	19 ± 7	9 ± 7
Fluoranthene	14 ± 8	880 ± 50	54 ± 7	350 ± 20
Pyrene	12 ± 5	870 ± 60	67 ± 7	360 ± 20
Benz(a)anthracene	<LOQ	330 ± 50	22 ± 7	100 ± 20
Chrysene	<LOQ	270 ± 10	15 ± 6	60 ± 10
Benzo(b)fluoranthene	ND	330 ± 40	<LOQ	70 ± 20
Benzo(k)fluoranthene	ND	200 ± 20	16 ± 6	52 ± 6
Benzo(a)pyrene	ND	270 ± 30	<LOQ	70 ± 10

ND = not determined.
LOQ = limit of quantitation.

extract showed that the difference was not due to the analytical performance. The main cause of the variability may have been the burning system; sampling conditions were never identical. Also, the sampling time may have influenced the results. Some of the results can be explained by the different particle mass of the samples: 30 nm ~1.7 μg/sample, 50 nm ~8 μg/sample, 70 nm ~14 μg/sample, 100 nm ~19 μg/sample. It needs to be added here that, in the case of aerosol MS (15 min collection), the particle

Table 4
Concentration of the target compounds in three different 70 nm size samples analyzed by GC × GC–TOFMS.

Compounds	Concentration (μg/L)		
	70 nm (Sample 1)	70 nm (Sample 2)	70 nm (Sample 3)
n-Alkanes			
Decane	41 ± 5	30 ± 5	33 ± 5
Dodecane	49 ± 2	47 ± 2	46 ± 2
Tetradecane	190 ± 10	150 ± 10	153 ± 10
Hexadecane	160 ± 10	34 ± 10	38 ± 10
Octadecane	300 ± 30	65 ± 8	88 ± 9
Eicosane	350 ± 20	68 ± 8	68 ± 8
Docosane	460 ± 20	130 ± 10	140 ± 10
Tetracosane	600 ± 20	120 ± 10	130 ± 10
Hexacosane	890 ± 90	140 ± 20	190 ± 20
Octacosane	550 ± 40	55 ± 6	90 ± 20
Triacontane	480 ± 50	57 ± 3	73 ± 3
PAHs			
Naphthalene	20 ± 6	11 ± 6	12 ± 6
Acenaphthylene	19 ± 4	10 ± 4	12 ± 4
Acenaphthene	11 ± 4	<LOQ	<LOQ
Fluorene	19 ± 4	9 ± 5	7 ± 5
Phenanthrene	52 ± 6	35 ± 6	12 ± 6
Anthracene	22 ± 4	7 ± 4	<LOQ
Carbazole	19 ± 7	<LOQ	<LOQ
Fluoranthene	54 ± 7	54 ± 7	19 ± 8
Pyrene	67 ± 7	53 ± 7	20 ± 4
Benz(a) anthracene	22 ± 7	<LOQ	<LOQ
Chrysene	15 ± 6	<LOQ	<LOQ
Benzo(b)fluoranthene	<LOQ	<LOQ	<LOQ
Benzo(k)fluoranthene	16 ± 6	ND	<LOQ
Benzo (a) pyrene	<LOQ	ND	<LOQ

ND = not determined.
LOQ = limit of quantitation.

masses were 30 nm ~5 ng/sample, 50 nm ~ 200 ng/sample, 70 nm ~1.3 μg/sample.

In our comparison of techniques, we conclude that the separation efficiency is higher in GC × GC than in conventional analyses with 1D GC. With a simple sample pre-treatment the GC × GC system provides a comprehensive picture of the sample. Moreover, the "structured" chromatograms that are obtained facilitate the recognition of unknowns and improve the reliability of the identification. The particle collection time required to obtain a representative sample for qualitative analysis was least with the aerosol MS. When the same collection times as in aerosol MS were tested with GC × GC–MS analyte amounts were under the detection limits.

The identification of compounds was best with the GC × GC system and most difficult with aerosol MS because library search could not be performed. Also the lack of chromatographic separation makes the analysis difficult. Aerosol MS was nevertheless a selective technique, and more sensitive for PAHs than for alkanes because of the better ionization efficiency for PAHs. Also liquid (standard) and aerosol samples behave differently due to their crystallization on the collection surface. Sensitivity was poorest for the GC–QMS technique but target compounds could still be identified in the samples. In general, it can be said that if our sampling system is to be used for ambient air measurements, where particle concentrations in the air are much lower, care must be taken to choose the appropriate analytical technique. When particle concentrations in the air are about 10^2–10^3 particles/cm^3 the collection times on filters will be several days, while the time to obtain a representative sample for aerosol MS is more like hours. To date, the ability of the aerosol MS techniques, in general, to provide quantitative information about sample compounds is limited. The technique is relatively new and not as well studied as conventional chromatographic techniques. There is still much to do to achieve the same quantitative level as in conventional mass spectrometric techniques. Moreover, our aerosol MS is a more limited technique because there is no possibility for MS–MS experiments. All in all, it is good to have a choice of different analytical techniques available, especially when samples are complex. Identification of the compounds will then be more reliable.

4. Conclusions

A new sampling technique with particle charging and size segregation was successfully applied in the analysis of wood combustion particles of selected sizes. All four analytical techniques employed (GC × GC–TOFMS, 1D GC–TOFMS, 1D GC–QMS, and aerosol MS) performed successfully. In the chromatographic techniques, particles were collected on a filter and analyzed off-line after sample preparation, whereas in aerosol MS the analysis was performed directly from the particle source. Although the individual samples varied widely due to irregular burning of the wood during the sampling, the results show that the developed sampling system is useful for this kind of analysis. The GC × GC–TOFMS provided the best separation efficiency and most reliable identification and quantitation of compounds. Collection and analysis times were shortest for aerosol MS, because the particle mass needed for the analysis was least. We conclude that all these techniques are useful for this type of analysis, and compound identification is more reliable when the results from different techniques can be combined.

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