

**In-situ derivatization
thermal desorption
GC-TOFMS**

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This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Technical Note: In-situ derivatization thermal desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species

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Received: 21 April 2011 – Accepted: 3 May 2011 – Published: 19 May 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

An in-situ derivatization thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS) was developed for determination of polar organic compounds. Hydroxyl and carboxyl groups of compounds such as anhydrous sugars, alcohols and phenols, fatty acids and resin acids are targets of the derivatization procedure. Derivatization is based on silylation with N-Methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) during the step of thermal desorption. The high temperature of 300 °C during desorption is utilized for the in-situ derivatization on the collection substrate (quartz fibre filters) accelerating the reaction rate. Thereby, the analysis time is as short as without derivatization. At first the filter surface is dampened with derivatization reagent before insertion of the sample into the thermal desorption unit. To ensure ongoing derivatization during thermal desorption the carrier gas is saturated with MSTFA until the desorption procedure is finished. The method introduced here was compared with direct thermal desorption gas chromatography time-of-flight-mass spectrometry (DTD-GC-TOFMS) and with solvent extraction (SE) procedures followed by gas chromatography and mass spectrometry. Comparisons were carried out with field samples originating from ambient aerosol collected on quartz fibre filters. Moreover, the methods have been applied on NIST Standard Reference Material Urban Dust (SRM 1649a).

1 Introduction

During the last decade direct thermal desorption (DTD) (someone like to prefer the term “thermal extraction”) methods were developed for quantification of semi volatile organic compounds (SVOC) adsorbed on ambient particulate matter (PM) (Falkovich and Rudich, 2001; Waterman et al., 2000). The advantage of DTD is the reduction of analyte losses and memory effects by desorption of the sample within the GC injector. In recent years an increasing number of samples had to be analysed for studying

ACPD

11, 15255–15295, 2011

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aerosol composition. Since a growing variety of organic compounds becomes more and more important for source apportionment (Dutton et al., 2009; Sklorz et al., 2007; Vedal et al., 2009), aerosol ageing studies and investigations on characteristics of particles responsible for climatic effects (Donahue et al., 2009) direct thermal desorption hyphenated with GC-MS can be a useful tool to deal daily sampling on long time series (Schnelle-Kreis et al., 2005a) or with high time resolution. Some research groups developed methods for direct thermal desorption for analysis of organic aerosol compounds in the past (Bates et al., 2008; Ding et al., 2009; Falkovich and Rudich, 2001; Gil-Moltó et al., 2009; Hays et al., 2003; Ho et al., 2008; Schnelle-Kreis et al., 2005b; van Drooge et al., 2009).

A recent development in thermal desorption techniques is the Thermal Desorption Aerosol GC-MS (TAG) (Lambe et al., 2010; Williams et al., 2006, 2010). Particle fractions are collected by humidifying and impaction into a thermal desorption cell. After a defined sampling time the organic matter is transferred to the gas chromatograph by thermal desorption. A high time resolution of one hour per sample and the chromatographic separation are the advantages of the TAG system.

Another development for thermal desorption of precipitated particulate matter is the methylation by tetramethylammonium hydroxide (TMAH) and its derivatives (Beiner et al., 2009; Fabbri et al., 2002) for quantification of organic acids. The applicability for other polar compounds is currently under investigation.

Polar organic substances are playing a major role in characterization of diverse atmospheric processes and also during formation of aerosols. The main organic combustion product of wood is the anhydrous sugar levoglucosan as a decomposition product of cellulose. This compound as well as its homologues mannosan and galactosan, decomposition products of hemi cellulose, are ubiquitous constituents of the atmosphere (Simoneit et al., 1999, 2004). Further wood combustion products originating from lignin breakdown or colophony can be observed. Most of them are of polar nature (Bari et al., 2009; Fine et al., 2001, 2002, 2004; Nolte et al., 2001). Another main source of polar organic compounds in the atmosphere are biogenic emissions. Not only sugars

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from plants, fungi and bacteria can be observed (Medeiros et al., 2006; Medeiros and Simoneit, 2007), but also huge amounts of unsaturated hydrocarbons are continuously evaporated by vegetation (Guenther et al., 1995; Kourtchev et al., 2005). Once organic substances are released to the atmosphere as gas or particle-bound they are exposed to UV radiation, radicals and oxidants. Depending on particle properties (e.g. pH value, possible reaction agents) reaction mechanisms and reaction velocities are affected. In ageing studies these facts are taken into account to investigate the formation of secondary organic aerosol (Hallquist et al., 2009). All of these reactions steadily increase the polarity of the reactants. Hence it is essential to integrate a derivatization step for observation of the polar organic tracers described and their behaviour immediately after combustion processes or in the atmosphere (Edney et al., 2003; Oliveira et al., 2007), e.g. supported by chamber experiments (Chiappini et al., 2006; Edney et al., 2005). Investigation of polar organic compounds is of great scientific interest due to their effect on particulate properties impacting climate processes. An increasing oxidation rate leads to acidification and growing of particles. The ongoing ageing is responsible for transformation of particles to cloud condensation nuclei (CCN).

In this work an in-situ derivatization thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS) is introduced combining short sampling time, powerful chromatographic separation and determination of polar organic substances. Good comparability of the thermal desorption method with a solvent extraction method can be ascertained. For inter comparison NIST Standard Reference Material Urban Dust SRM 1649a (National Institute of Standards and Technology, USA) was employed to validate the method for analysis of polycyclic hydrocarbons (Bates et al., 2008; Falkovich and Rudich, 2001; Gil-Moltó et al., 2009; Ho et al., 2008; van Drooge et al., 2009; Waterman et al., 2000, 2001). Levoglucosan, mannosan and galactosan were determined in the standard reference material and compared to results already published by Kuo et al. (2008), Larsen et al. (2006) and Louchouart et al. (2009). Comparison of different methods for analysis of ambient aerosol samples was carried out, too, (Ho and Yu, 2004, 2008; Ma et al., 2010; van

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Drooge et al., 2009) concerning polar substances, polycyclic aromatic hydrocarbons (PAH) and oxidized polycyclic hydrocarbons (o-PAH). PAH and even more o-PAH are delicate analytes due to generate artefacts during sampling, sample preparation and analysis (Liu et al., 2006). Therefore, analysis methods for these substance classes have to be validated properly. The direct thermal desorption (DTD) method presented here as a reference method was already introduced in former papers by Schnelle-Kreis et al. (2005a,b, 2007). Here the accuracy of this method is demonstrated briefly.

2 Experimental

2.1 Sampling of ambient aerosol

Prior to sampling quartz fibre filters were baked for at least eight hours at 550 °C to remove all organic matter. The sampler was located at the aerosol characterization site of the Helmholtz Zentrum München at the University of Applied Sciences, Augsburg, next to the inner city of Augsburg, Germany (UAS, urban background). Samples were taken from 1 March 2010 to 14 March 2010.

For chemical analysis PM_{2.5} samples were collected with a low volume sequential sampler (Partisol-Plus Model 2025, Rupprecht & Patashnick, NY, USA) on quartz fibre filters (T293, Munktell, Grycksbo, Sweden) at a flow rate of 16.7 l min⁻¹. Sampling time was 24 h, thus airborne particulate matter of 24 m³ of air was collected on each filter. The samples were stored in glass containers at -18 °C until analysis. Filters for solvent extraction were extracted directly after sampling.

2.2 Basics of in-situ derivatization and thermal desorption (IDTD)

The enhanced IDTD method involves the option to quantify polar constituents of organic particulate matter. The method presented allows derivatization of the polar organic fraction of filter samples in-situ on the filter during thermal desorption. Derivatization and desorption of polar organic compounds occurs directly from particulate

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matter on the filters. The advantages of a direct thermal desorption system employed for this study are: (1) direct placement of samples in the GC liner, so called in-injector thermal desorption avoiding sample transfer lines frequently causing cold spots, (2) the possibility of automatic liner exchange, (3) rapid heating rates of the injector and (4) replacement of the GC liner for every sample.

The derivatization procedure consists of two steps and is fully automated with an applicable sampling robot. The first step is the addition of the derivatization reagent N-Methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) for complete moistening of filter and particulate matter. The second step is very important for quantitative silylation of polar organic compounds by MSTFA. The carrier gas is saturated with derivatization reagent by switching to a second pathway leading over a cartridge filled with MSTFA during the thermal desorption process (Fig. 1). The high temperature of 300 °C during desorption increases derivatization rate sufficiently without additional catalyst.

The in-situ derivatization thermal desorption GC-TOFMS (IDTD-GC-TOFMS) was employed for the main anhydrous sugars levoglucosan, galactosan and mannosan occurring in ambient aerosol and further highly polar organic compounds like resin acids and lignin combustion products. Analysis of levoglucosan is possible by many different methods published in a variety of papers. An overview of detection and quantification of levoglucosan in atmospheric aerosols is given by the review of Schkolnik and Rudich (2006). As a conclusion of these studies we can find that the choice of solvent or solvent mixture is most crucial for methods using solvent extraction (Louchouart et al., 2009). The polarity of the extraction solvent constitutes a limiting factor for the extraction yield of levoglucosan. To determine all substance classes being of interest for studying ambient aerosol it may be necessary to extract different polar fractions by different solvents. The advantage of the described in-situ derivatization thermal desorption method is minimization of the working steps, avoiding handling with different solvent mixtures and making even highly polar substances ascertainable. An overview of the compound classes analysed is shown in Fig. 2 in terms of single ion chromatograms.

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2.3 Sample preparation, in-situ derivatization and thermal desorption

For analysis of particulate matter collected the filters were cut by a special tool into filter aliquots which were stripes of the dimension 13.5 mm × 2 mm. One filter stripe (sample aliquot of 0.55 m³ of sampled air) was spiked with two internal standard mixtures (isotope-labelled reference compounds) for quantification. The first (non polar) internal standard consisted of fifteen deuterated PAH, two deuterated o-PAH and four deuterated alkanes. D₈-9,10-anthracenedione and D₁₀-benz[a]anthracene-7,12-dione were synthesized in our laboratory (Liu et al., 2006) (see Table 1 for detailed description and concentrations). The second (polar) internal standard mixture contained ¹³C₆-levoglucosan (Omicron Biochemicals, USA), ¹³C₆-vanillin (Larodan, Sweden) and D₃₁-palmitic acid (CIL, USA). Samples were placed into goose-neck glass-liners for thermal desorption which were sealed with PTFE caps. Further treatments were carried out by the sampling robot. Prior to analysis liners were opened and 10 µl MSTFA (Macherey-Nagel, Germany) was added in each liner to moisten the filter surface.

For analysis of the NIST Standard Reference Material Urban Dust 1649a portions of 0.06 mg were thermally desorbed. Due to the small amount required the urban dust was mixed and homogenized first with sodium sulphate (w/w, 1/1000) which was annealed and ground before. The GC injection liners were loaded with 60 mg of this mixture. Isotope-labelled standards were added to this mixture. The liners were sealed with PTFE caps until analysis. As described for filter samples MSTFA was injected right before analysis.

Liners were placed into a direct (in-injector) thermal desorption unit (Optic 3, Atas GL, Netherlands) mounted on the gas chromatograph. An automated sampling robot (Focus, Atas GL, Netherlands) exchanged the complete GC liners placed in the injector which was automatically closed and opened by a liner exchanging unit (Linex, Atas GL, Netherlands). For each sample a freshly deactivated GC liner was used. Deactivation was done by annealing the liners at 550 °C for at least twelve hours followed by a derivatization treatment of the glass surface with chlorotrimethylsilan (TMCS, Merck,

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Germany) for further twelve hours. A glass wool plug above the goose-neck prevented particles from the filter to enter the capillary column.

After liners were placed into the cold injector (60 °C) a steady flow of carrier gas (helium) removed the air. During this venting step of 60 s carrier gas flow was 0.7 ml min⁻¹, split flow was 50 ml min⁻¹. After 180 s carrier gas flow was increased split less to 4 ml min⁻¹. The carrier gas was lead to a bypass with a cartridge filled with MSTFA before entering the injector. This bypass was opened and closed via two 3-port/2-way solenoid valves being controlled by the Optic software and hardware unit (Atas GL, Netherlands). During opened bypass the carrier gas was saturated with MSTFA. The injector was heated up to 300 °C with a heating rate of 2 °C s⁻¹. During 16 min of reaction and desorption time the carrier gas was continuously saturated with derivatization reagent (Fig. 1). Subsequently the bypass was closed and the column flow was set to 0.7 l min⁻¹ with a split flow of 50 l min⁻¹.

2.4 Gas chromatography and time-of-flight mass spectrometry

Desorbed molecules were focused at 70 °C on the head of the capillary column, BPX5, 25 m, 0.22 mm ID, 0.25 μm film (SGE, Australia) which was installed in an Agilent 6890 gas chromatograph (Agilent, USA). The thermal desorption step was followed by heating up the GC oven to 130 °C with a rate of 80 °C min⁻¹. Then the rate was lowered to 8 °C min⁻¹ until a temperature of 330 °C was reached followed by an isothermal time of 30 min.

Identification and quantification of target compounds were carried out on a Pegasus III TOFMS using Chroma TOF software package (LECO, USA) being capable of peak deconvolution. The data acquisition range was *m/z* 35 to 500 with an acquisition frequency of 25 spectra per second which is necessary for reliable peak deconvolution.

Analytes which were not available as standard in analytical grade were identified by their mass spectra and the retention time index. In those cases quantification was achieved with an adequate surrogate standard on semi quantitative basis. Surrogates are specified in Table 1.

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Calibration of thermal desorption was carried out applying standard addition to reference filters (PM samples). These filters were spiked with internal standard and derivatization standard, respectively. Standard mixtures with native organic compounds were added to the reference filters in different concentration levels (for calibration ranges see Table 2).

2.5 Calibration of thermal desorption

The calibration of the thermal desorption method was carried out applying standard addition to reference filters (PM samples). These filters were spiked with internal standard and derivatization standard, respectively. Standard mixtures with native organic compounds were added to the reference filters in different concentration levels (for calibration ranges see Table 2).

2.6 Direct thermal desorption (DTD)

DTD was described in detail elsewhere (Schnelle-Kreis et al., 2005a,b, 2007). The pre-treatment of filters and liners for DTD was identical as described above without adding the isotope-labelled standard mixture of polar compounds. The vent time before thermal desorption was shorter (one minute) and the carrier gas was not treated with derivatization reagent during thermal desorption process.

2.7 Solvent extraction of non-polar compounds

The method for solvent extraction of non-polar compounds was described elsewhere (Liu et al., 2006; Sklorz et al., 2007). Extraction was carried out utilizing soxhlet extraction with dichloromethane as solvent. Therefore, filters or a mixture of SRM 1649a and sodium sulphate were placed in fritted soxhlet sleeves made of glass. Soxhlet extraction time was 16 h with at least six cycles per hour. Extracts were dried over pre-baked sodium sulphate and filtrated to remove filter residues. Extracts were concentrated to 1 ml and additionally cleaned up and fractionated on a liquid chromatography

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column packed with silica (Promochem, Germany) deactivated with three percent of water. The first fraction eluted with hexane/dichloromethane (9:1, v/v) (all solvents: Merck, Germany) containing the non-polar components like alkanes was not analysed. The second and third fraction eluted with hexane/dichloromethane (1:1, v/v) and dichloromethane/methanol (19:1, v/v) containing PAH and o-PAH were combined for analysis. The mixtures were concentrated to adjust the concentrations of the analytes to the same range as applied for DTD (one injection equates to 1 m³ of sampled air). Samples were analysed by GC-HRMS.

The chromatographic separation for solvent extracted (SE) samples was carried out on a Varian GC 3400 (Varian, USA) assembled with a retention gap (guard column), deactivated fused silica, 2.5 m, 0.22 mm ID (SGE) and a BPX5 column, 25 m, 0.22 mm ID, 0.25 µm film (SGE). The sector field mass spectrometer MAT95 (Thermo Scientific, Germany) was operated in multiple ion detection mode (MID) for target analysis.

2.8 Solvent extraction of polar compounds

Solvent extraction of polar compounds was carried out with dichloromethane/methanol (1:1, v/v) in an ultrasonic bath. Prior to extraction the samples were spiked with internal standard mixtures. Ultrasonication was carried out three times with five millilitres of solvent for fifteen minutes each. The three extracts were combined and filtered over PTFE syringe membrane filters (0.2 µm, Sartorius, Germany). Solvent was evaporated to dryness. Derivatization was started by adding MSTFA to the samples. Reaction time was 3 h at 80 °C. Samples were measured with the same GC-TOFMS equipment as described above for IDTD-GC-TOFMS which was also used for thermal desorption. The injector employed was also capable of liquid injection (here one injection equates to 0.5–1 m³ of sampled air). The GC method was programmed as follows: injector temperature: 300 °C, oven temperature: 100 °C for 1 min. Heating rates were 25 °C min⁻¹ to 175 °C followed by a rate of 5 °C min⁻¹ to 330 °C with an isothermal of 15 min at 330 °C at the end of the run.

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Calibration for liquid extraction samples was carried out by evaporating different standard dilutions to dryness. MSTFA was added directly to the dried standard. The further procedure was like the sample treatment.

3 Results and discussion

3.1 Derivatization

MSTFA as silylation reagent for the IDTD method has the advantage that it is not necessary to be removed from the sample before GC-MS analysis. The products of MSTFA reactions exhibit high vapour pressures. On non-polar capillary columns MSTFA has characteristics like many other solvents being used for solvent injection in GC-MS. Thus short retention times with sharp solvent peaks without carry over are achievable. At usual conditions (e.g. temperature of 80 °C) MSTFA is reacting relatively slow. Sterically hindered molecules exhibit poor reaction yields with MSTFA. For that reason a catalyst like chlorotrimethylsilan (TMCS) which acts as Lewis acid may be used to accelerate the reaction. Combinations such as BSTFA (N,N'-bistrimethylsilyltrifluoroacetamide) and TMCS (99/1, v/v) or MSTFA and TMCS (99/1, v/v) are widely used for derivatization particularly for determination of levoglucosan and other polar compounds in atmospheric aerosol (Nolte et al., 2001; Simoneit et al., 1999; Zdrahal et al., 2002). Due to a large polar organic fraction and inorganic salts ambient aerosol samples also contain water. Water is also involved in reactions with silylation reagents. This leads to two essentials for derivatization reaction with ambient aerosol: first, a sufficient surplus of derivatization agent is necessary and second, TMCS has to be excluded for in-situ reactions in the gas chromatography system. Poor column life time could be a result of high reaction yields of HCl formed by water and TMCS. To accelerate the reaction an increase of temperature can be applied instead of catalysts. In the method presented the high temperatures of thermal desorption increase reaction speed and yields. A verification of derivatization yields was done by comparison

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of responses of isotope-labelled standards generated with the IDTD method and with directly derivatized standard solution as used for the here described calibration curves of SE methods. Therefore, a recovery efficiency standard (D₄₂-eicosane) was added to the samples prior to injection. Assuming that derivatization reactions in solution were complete (100 %) the yields for IDTD were calculated relative to yields of derivatization in solution. The derivatization yields of vanillin (111 %), levoglucosan (97 %) and palmitic acid (107 %) suggest that reactions of both methods are comparable.

Due to possible degradation reactions of polar organic compounds at high temperatures the first derivatization step (the moistening of the filter with MSTFA) was introduced as described before to start the reaction and to protect the compounds until the MSTFA-saturated helium enters the injection port of the gas chromatograph. The enrichment of carrier gas with volatile derivatization reagent has several advantages. (1) A steady flow of MSTFA during thermal desorption protects derivatized polar organic compounds from degradation until the transfer to the gas chromatograph is completed. (2) Derivatization products are removed immediately from the reaction medium. (3) Equilibrium can be prevented and a high yield of conversion is possible. (4) The surplus of MSTFA is maintained until derivatization and thermal desorption are finalized. (5) An improvement of response of components suspected to be sensitive for artefact formation at thermal desorption conditions can be recognized. For instance, low volatile PAH like benzopyrenes and perylene showed a higher response when the MSTFA saturated carrier gas flow was switched on during thermal desorption even without moistening of the filters with MSTFA before thermal desorption. The explanation for this effect is the deactivation of active surfaces e.g. on the quartz fibres. Figure 3 shows an example for a low volume ambient aerosol sample (200 l of sampled air) spiked with isotope labelled standard substances when measured with and without MSTFA-saturated carrier gas. The example was taken from a series of PM₁ filter samples with sampling on hourly basis. The PM deposits on the filters were quite low. Therefore, a larger part of the filter sample was applied for thermal desorption (108 mm² in contrast to 27 mm² for 24 h samples). A two-fold response improvement was found for some compounds when

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working with MSTFA saturated carrier gas. This was especially the case for the reactive compounds benz[a]pyrene and perylene without affecting quantification results. The positive effect (resulting in a lower limit of quantification (LOQ)) was verified by eighteen additional samples of PM₁ filter samples collected hourly.

Nevertheless, MSTFA may also be responsible for some artefacts like adducts with aldehydes (Blau and King, 1977; Halket and Zaikin, 2003; Little, 1999). Derivatization adducts are formed by enols originating from aldehydes with an α -hydrogen atom. Electron impact mass spectra therefore show ions with fragments at m/z 228 (C₇H₁₃O₂NF₃Si⁺) and m/z 184 (C₅H₉ONF₃Si⁺). For aromatic aldehydes like vanillin, coniferyl aldehyde and syringyl aldehyde, however, no formation of adducts was observed.

3.2 Calibration

Calibration curves of IDTD were very similar to the solvent extraction method. Precision is better for calibration curves of SE due to the fact that standard solutions were directly used for calibration. Whereas for thermal desorption methods calibration reasonably is carried out by standard addition to reference filters. Thus response differences due to matrix effects are minimized. For that reason some calibration regressions exhibit a considerable offset. The intercept depends on the concentration of components on the reference filters. Regression curve data are specified in Table 2.

Calibrations were done with the according isotope-labelled standards and the native compounds with high purity as far as possible (Table 1). Only three different isotope-labelled polar substances were applicable, namely ¹³C₆-vanillin, ¹³C₆-levoglucosan and D₃₁-palmitic acid. As most substances analysed here were available in sufficient purity, only an isotope-labelled internal surrogate standard had to be applied. However, some substances described here (e.g. dehydroabietic acid, syringyl aldehyde, divanillyl) were not available in sufficient purity. Moreover, no isotope-labelled analogues were available. Thus, only semi-quantitative results using surrogates were obtained for these compounds. Applied surrogates are specified in Table 1, too. Due to different

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responses of compounds caused by different extraction and derivatization yields the range of application of isotope-labelled compounds as internal standard for further substances is limited. Moreover, those compounds should exhibit equal chromatographic properties and similar fragmentation characteristics when treated by electron-impact ionization. For these reasons only compounds very similar to the anhydrous sugars levoglucosan, mannosan and galactosan can be quantified properly with $^{13}\text{C}_6$ -levoglucosan as internal standard. D_{31} -palmitic acid was used mainly for acids, aldehydes and ketones. Even some deuterated PAH were used as internal standard for some polar compounds characterized by a two-ring (divanillyl) or three-ring structure (isopimaric acid). $^{13}\text{C}_6$ -vanillin was used as standard only for its native form. Experiments with vanillic acid and vanillic acid methyl ester were not successful in receiving an adequate calibration curve with $^{13}\text{C}_6$ -vanillin as internal standard.

Levoglucosan showed good linearity in calibration curves over the whole working range of 3.5–350 ng Levoglucosan per analysis. The slope is similar to that of the calibration curve of the solvent extraction method shown in Table 2. It also shows the intercept of the IDTD method caused by standard addition to a reference sample. The precision of both methods is quite good: 6% for thermal desorption and 4% for SE. The limit of detection is somewhat higher for IDTD compared to SE (0.6 ng and 0.1 ng, respectively).

Other polar compounds than levoglucosan exhibit good linear fittings, too. However, sensitivity of some polar compounds is quite poor, especially for small molecules like succinic acid, malic acid, or guaiacol. Therefore, Table 2 shows the calibration data of malic acid as an example for these compounds with a relative low slope of 0.033 compared to 0.228 for the solvent extraction method. This short chain multifunctional acid is also discussed in the comparison of the methods applied for ambient aerosol samples. Anyhow, correlation of quantitative results from IDTD with the solvent extraction method is quite good. Precision for malic acid for both methods was near 10%. Some compounds in low concentrations exhibit higher variation coefficients up to 17%, especially syringic acid (16%) and vanillic acid methyl ester (17%).

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Polycyclic aromatic hydrocarbons (PAH) and oxidized PAH (o-PAH) are not affected by the derivatization procedure. Most calibration regression curves are showing good linearity with similar sensitivities for IDTD and SE. No generation of artefacts were observed neither when comparing the in-situ derivatization procedure with the usual thermal desorption procedure nor when comparing both thermal desorption methods with a solvent extraction procedure. Moreover, the calibrations of the thermal desorption methods were almost applicable for solvent extraction methods. Only anthracene shows variation coefficients higher than 10% induced by the poor response of anthracene in GC-MS. Other PAH exhibit variation coefficients below 10%. This is because of the application of the respective isotope-labelled standards for each PAH (Table 1). For o-PAH similar observations were made. 9,10-Anthracenedione and benzo[a]anthracene-7,12-dione have low variation coefficients (2% and 9%, respectively). For these two o-PAH the according isotope-labelled standards were applied. Especially 9H-fluoren-9-one and cyclopenta[def]phenanthrene show higher variations though adequate isotope-labelled surrogates were used. D₁₀-phenanthrene and D₁₂-benzo[a]anthracene were used in these cases due to best regression fittings.

3.3 Comparison of methods based on the analysis of SRM 1649a

The DTD method was employed in studies already published by Schnelle-Kreis et al. (2005a, b, 2007). The standard deviation of results ($n = 5$) for all compounds with DTD was smaller than 20% except for perylene and anthracene which were near the limits of detection. This is due to their low content in the reference material and the small amount of about 60 µg which was used for thermal desorption (this means a total mass of anthracene of 26 pg and 39 pg of perylene, respectively). Similar effects were described by van Drooge et al. (2009). More crucial seems the fact that the concentrations of benzo[a]pyrene, an important marker for several emission sources and with high carcinogenic potential, were overestimated by 40% of the certified value. This phenomenon was not observed when using the IDTD method. We suggest that the deactivation of substrate may be also responsible for lower affection of some PAH as

described for the quartz fibres before. Especially benzo[a]pyrene and perylene seem to be susceptible for degradation of spiked internal standards.

Nevertheless, the results are satisfying with respect to the low amounts of SRM in analysis. Other studies used at least 500 μg (Gil-Moltó et al., 2009), 900 μg up to 1.9 mg (Ho et al., 2008), or 3 mg (Waterman et al., 2000) of urban dust for thermal desorption. Only van Drooge et al. analysed lower SRM 1649a quantities (van Drooge et al., 2009) ranging from 60 μg to 550 μg . Results are visualized in Table 3 and Fig. 4.

The concentration of levoglucosan contained in SRM 1649a was already measured and published (Kuo et al., 2008; Larsen et al., 2006; Louchouart et al., 2009). Although the standard reference materials were not certified for levoglucosan it is possible to use them for laboratory inter comparison. In this study a determination of levoglucosan and its analogues mannosan and galactosan was carried out the same way as for filter samples with IDTD. Measured values for levoglucosan were comparable with values already published (Table 4). Concentrations of mannosan and galactosan have only been published by Louchouart et al. (2009). Our results for mannosan were comparable with the published, whereas the concentrations of galactosan were more than two times higher (10.8 $\mu\text{g g}^{-1}$ in this study and 5.0 $\mu\text{g g}^{-1}$ found by Louchouart et al., respectively). The main difference of the methods is the manner of extraction. Louchouart et al. employed a pressurized fluid extraction with an accelerated solvent extraction system. Due to the similarity of the anhydrous sugars we doubt that this difference could be an extraction artefact. The observed ratio of levoglucosan/mannosan/galactosan was similar as found for ambient aerosol by Ma et al. (15:3:1 v/v/v) (Ma et al., 2010).

3.4 Comparison of the methods based on ambient aerosol samples

A comparison of the in-situ derivatization thermal desorption method and an ultrasonic extracting method followed by a derivatization step in solution (SE) was carried out. Correlations of quantitative results are demonstrated. This is visualized by plotting the result of IDTD analysis against concentrations determined by solvent extraction

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(x-axis). A slope higher than one and a positive offset are indicating higher concentrations resulting from thermal desorption whereas a slope smaller than one and a negative offset are caused by higher concentrations found by solvent extracted samples. Therefore, a good comparability is indicated by a regression with a slope near one and an axis intercept at the point of origin. The comparability is not influenced by slope and offset, but by the precision of both methods indicated by the correlation coefficient.

Both methods show good comparability for most PAH (Fig. 5a). The correlations indicate good linearity with a slope of nearly one or slightly higher with the exception of phenanthrene and perylene. These compounds showed higher concentrations when analysed by solvent extraction. Usually phenanthrene and anthracene exhibit higher variations due to their low boiling point and low concentration in the particulate phase. Nevertheless, correlation of DTD and SE was quite good. The data of fluoranthene and pyrene exhibited the highest correlation of all PAH analysed, whereas for benzo[a]anthracene, chrysene, triphenylene and the benzofluoranthenes up to 25 % higher concentrations were determined with IDTD. Retene exhibited a good comparability but a somewhat lower correlation coefficient. Experiences indicate higher variations of retene when analysed by thermal desorption methods. Benzo[a]pyrene which is known to be more reactive showed no difference in behaviour compared to benzo[e]pyrene. These benzopyrenes showed higher concentrations when analysed by thermal desorption. The lower concentrations of perylene when analysed by IDTD may be a result of low concentrations of perylene in ambient aerosol samples being also indicated by a poor correlation coefficient. Indeno[1,2,3-cd]pyrene showed good comparability but with somewhat higher variations. Benzo[ghi]perylene showed concentrations more than 30 % higher when analysed by IDTD.

Comparability of the analytical methods is also demonstrated for oxidized PAH (Fig. 5b). Variations of the results were somewhat higher than for PAH. For o-PAH only two isotope-labelled standards were applied. The higher variation coefficients of calibration curves indicate a lower precision of analysis of o-PAH for both methods. An influence on analysis of field samples is therefore not avoidable. 9H-fluoren-9-one

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and 11H-benzo[b]fluoren-11-one showed good correlation and a slope near unity for the comparison of IDTD and SE. Despite of its high variation coefficient of the calibration curve fitting 9H-fluoren-9-one showed good comparability. On the other hand higher values of other o-PAH determined were observed when being analysed by the in-situ derivatization thermal desorption. 9,10-Anthracenedione, 1,4-naphthalic anhydride, cyclopenta[def]phenanthren-4-one and 11H-benzo[a]fluoren-11-one showed similar correlation coefficients but concentrations were at least 30 % higher when analysed with IDTD compared to SE. Neither a loss of analytes by solvent extraction nor a generation of o-PAH from PAH at thermal desorption conditions can be excluded. An underestimation of analyte concentrations determined by solvent extraction seems to be possible as a result of a different extraction efficiency of spiked standards and native sample compounds.

For selected polar organic compounds, especially wood combustion tracers, IDTD was applied to ambient aerosol samples, the results being compared with SE. For all compounds with concentrations above the limit of detection (LOD) in most collected ambient aerosol samples the correlation to solvent extracted ones is demonstrated (Fig. 5c). A good correlation and a slope near unity were found for levoglucosan. The correlations for its isomers galactosan and mannosan were not as good by far. Due to sterical advantages of levoglucosan in forming silylation products it can be assumed that derivatization yields were higher for levoglucosan compared to those of mannosan and galactosan.

The resin derived compounds dehydroabietic acid and dehydroabietic acid methyl ester were other compounds being present in all ambient aerosol samples. These compounds are reaction products of wood combustion generated by dehydrogenation and oxidation of resin acids originating from colophony of conifers (Leithead et al., 2006; Nolte et al., 2002). Both substances were quantified using D₁₀-pyrene as internal standard. Isopimaric acid was used as surrogate for external calibration of dehydroabietic acid. Pyrene was used for external calibration of dehydroabietic acid methyl ester already exhibiting a protected carboxylic group and therefore not being affected

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by derivatization. The results for dehydroabietic acid, dehydroabietic acid methyl ester and abietic acid showed up to two times higher values when analysed by IDTD. Correlations are not even roughly as good as for substances with according isotope-labelled internal standard but were still acceptable. But correlation coefficients were in the same range like the other resin acids abietic acid and isopimaric acid. These acids were calibrated using respective standards. Here the lower correlation coefficients were a result of low concentrations in ambient aerosol.

Beside levoglucosan especially for the relatively small acids syringic acid, phthalic acid and malic acid a good consistency of the two methods could be observed. On the other hand twofold higher concentrations of the lignin combustion products acetosyringone, vanillic acid and divanillyl were found when analysed by IDTD-GC-TOFMS, as was the case for dehydroabietic acid. An interesting fact is the lack of consistency for syringic acid and vanillic acid. These similar molecules exhibited different results when analysed with IDTD and SE. Both acids were calibrated and analysed by applying D₃₁-palmitic acid as internal standard (Table 1).

Experiments with different isotope-labelled standards substantiate the suspicion that in some cases extraction efficiency was poor when using ultrasonic-assisted extraction in dichloromethane/methanol (1/1, v/v). The use of this solvent mixture is a compromise to achieve sufficient extraction yields of all analytes. Otherwise different fractions have to be extracted by different solvents requiring additional work for sample work-up. Despite of better precision of calibration curves of SE as shown in Table 2 it must be noticed that calibration regression fittings were calculated on two different ways. The standard addition as used for IDTD for calculation of regression curves already comprises the extraction efficiencies, whereas the calibration data of the SE method are based on derivatized standard compounds. Indeed, IDTD calibration curves for vanillic acid, acetosyringone, isopimaric acid and dehydroabietic acid showed less sensitivity compared to SE. In these cases a correction by recovery calculation is not possible due to non reliable isotope-labelled standards. PAH also showed a tendency to be underestimated in concentration when analysed by the SE method. This deviation

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increased with increasing boiling point of the PAH. Due to a high number of according isotope-labelled standards it is not as present as for other substances by far.

The correlation experiments showed a good consistency of the analysis methods for malic acid, mannosan, levoglucosan, phthalic acid, syringic acid and isopimaric acid, 9H-fluoren-9-one, 11H-benzo[b]fluoren-11-one and the most PAH. A good consistency for other substances was opposed by the use of internal surrogate standards which were not isotope-labelled analogues of the analytes. Dehydroabietic acid methyl ester demonstrates that this is not only a drawback of polar substances even though measured concentrations of the methyl ester were somewhat lower than those of the free acid. On the other hand derivatization yields were similar for both methods.

4 Conclusions

A fast in-situ derivatization thermal desorption technique was developed for GC-MS. This method is able to deal with daily ambient aerosol sampling. The feature of analysing polar compounds gets more and more important to characterize ambient aerosol supporting source apportionment studies and aerosol ageing studies, even those employing chamber experiments (Böge et al., 2006; Chandramouli et al., 2003; Edney et al., 2005). As an amplification of this method GCxGC-techniques (Goldstein et al., 2008; Ma and Hays, 2008; Schnelle-Kreis et al., 2005b) could deal with enlarged data quantities and reduces peak co-elution significantly. Although the LecoCromaTOF[®]-Software has a powerful deconvolution algorithm peak separation becomes a problem for chromatograms including additional silylation products. Nevertheless, one dimensional gas chromatography in combination with derivatization techniques provides more relevant information of the chemical properties of ambient aerosol than without derivatization.

A positive side effect demonstrated is the minimization of matrix effects by deactivation of active quartz fibres caused by the use of MSTFA during thermal desorption. An improvement of LOD/LOQ for PAH was shown and could also be suggested for further analytes.

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The advantages of isotope-labelled standards in GC-MS are well known. They gain an even higher importance for thermal desorption methods. The response of organic compounds depends on the composition of the particle matrix and on the quartz fibres. Compared to solvent extraction not only a fraction of this matrix but the whole sample composition affects the analysis. This always should be kept in mind when applying thermal desorption techniques. It is strictly recommended to employ a large set of isotope-labelled standards. Even compounds like PAH and dehydroabietic methyl ester do not exhibit responses proportional to reasonable surrogates, as shown in this paper. Nevertheless, the measured concentration of these compounds may be more affected by sampling artefacts than by the analysis methods employed. We clearly demonstrated that in-situ derivatization thermal desorption gas chromatography time-of-flight mass spectrometry shows a good linearity and sensitivity over nearly one order of magnitude for analysis of the important and relatively stable biomass marker levoglucosan.

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Table 1. Analytes, internal standards and surrogates employed for DTD- and IDTD-GC-TOFMS. A surrogate is only specified when no native standard was available for calibration. Thus, only semi-quantification was achievable for these analytes. Benzofluoranthenes were not chromatographically separated (sum of benzo[b]-, benzo[j]- and benzo[k]fluoranthene).

Analyte	Internal Standard	Surrogate	<i>m/z</i> used for quantification	Concentration of internal standard (ng)
Phenanthrene	Phenanthrene-d ₁₀		178/188	3.45
Anthracene	Anthracene-d ₁₀		178/188	0.461
Fluoranthene	Fluoranthene-d ₁₀		202/212	0.681
Pyrene	Pyrene-d ₁₀		202/212	1.68
Benzo[a]anthracene	Benzo[a]anthracene-d ₁₂		228/240	0.962
Chrysene	Chrysene-d ₁₂		228/240	0.962
sum Benzofluoranthenes	Benzo[b]fluoranthene-d ₁₂	Benzo[b]fluoranthene	252/264	0.802
Benzo[e]pyrene	Benzo[e]pyrene-d ₁₂		252/264	0.802
Benzo[a]pyrene	Benzo[a]pyrene-d ₁₂		252/264	1.04
Perylene	Perylene-d ₁₂		252/264	1.12
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene-d ₁₂		276/288	0.721
Dibenzo[ah]anthracene	Dibenzo[ah]anthracene-d ₁₄		278/292	0.842
Benzo[ghi]perylene	Benzo[ghi]perylene-d ₁₂		276/288	2.00
Coronene	Coronene-d ₁₂		300/312	0.641
9H-Fluoren-9-one	Phenanthrene-d ₁₀		180/188	3.45
9,10-Anthracenedione	9,10-Anthracenedione-d ₈		180/188	1.89
1,8-Naphthalic anhydride	9,10-Anthracenedione-d ₈		154/162	1.89
Cyclopenta[def]phenanthrenone	Benzo[a]anthracene-d ₁₂		204/240	0.962
11H-Benzo[a]fluoren-11-one	Benzo[a]anthracene-d ₁₂		230/240	0.962
11H-Benzo[b]fluoren-11-one	Benzo[a]anthracene-d ₁₂		230/240	0.962
Benzo[a]anthracene-7,12-dione	Benzo[a]anthracene-7,12-dione-d ₁₀		258/268	1.92

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Table 1. Continued.

Analyte	Internal Standard	Surrogate	<i>m/z</i> used for quantification	Concentration of internal standard (ng)
Malic acid	Palmitic acid-d ₃₁		233/344	60.8
Vanillin	Vanillin- ¹³ C ₆		194/200	15.6
Galactosan	Levoglucozan- ¹³ C ₆		217/220	60.8
Mannosan	Levoglucozan- ¹³ C ₆		217/220	60.8
Levoglucozan	Levoglucozan- ¹³ C ₆		217/220	60.8
Phthalic acid	Levoglucozan- ¹³ C ₆		295/338	60.8
Vanillic acid methyl ester	Palmitic acid-d ₃₁		224/344	12.6
Vanillic acid	Palmitic acid-d ₃₁		297/344	12.6
Syringic acid	Palmitic acid-d ₃₁		327/344	12.6
Syringyl aldehyde	Palmitic acid-d ₃₁	Acetosyringone	224/344	12.6
Acetosyringone	Palmitic acid-d ₃₁		238/344	12.6
Syringylacetone	Levoglucozan- ¹³ C ₆		239/338	60.8
Retene	Benzo[a]anthracene-d ₁₂	Benzo[a]anthracene	219/240	0.962
Isopimaric acid	Benzo[a]anthracene-d ₁₂		241/240	0.962
Dehydroabietic acid methyl ester	Pyrene-d ₁₀	Pyrene	299/212	1.68
Dehydroabietic acid	Pyrene-d ₁₀	Isopimaric acid	239/212	1.68
Abietic acid	Palmitic acid-d ₃₁		256/344	12.6
7-Oxodehydroabietic acid	Benzo[a]anthracene-d ₁₂	Isopimaric acid	253/240	12.6
Divanillyl	Pyrene-d ₁₀	Pyrene	239/212	1.68

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Table 2a. Validation parameters obtained from the calibration curves of IDTD-GC-TOF MS. Calibration range means lowest and highest standard concentrations used for the calibration curve; a = interception, b = slope (area ratio/mass ratio).

Analyte	Calibration range (ng)	a	b	R^2	Precision	LOD (ng)	LOQ (ng)
Phenanthrene	0.790–39.5	0.044	1.148	0.999	3%	0.019	0.057
Anthracene	0.212–10.6	−0.132	1.789	0.983	15%	0.558	1.67
Fluoranthene	0.283–14.1	0.050	1.403	0.998	5%	0.058	0.174
Pyrene	0.392–19.6	0.007	1.315	1.000	1%	0.001	0.004
Benzo[a]anthracene	0.290–14.5	−0.217	1.871	0.997	7%	0.087	0.260
Chrysene	0.277–13.8	0.018	0.534	0.998	5%	0.016	0.049
sum Benzofluoranthenes	0.098–4.89	0.017	0.805	1.000	2%	0.001	0.002
Benzo[e]pyrene	0.134–6.71	−0.021	1.523	1.000	2%	0.002	0.005
Benzo[a]pyrene	0.130–6.49	−0.010	1.384	0.999	4%	0.005	0.016
Perylene	0.070–3.52	−0.092	1.510	0.996	7%	0.005	0.014
Indeno[1,2,3-cd]pyrene	0.069–3.44	0.139	0.850	0.996	6%	0.005	0.015
Dibenzo[ah]anthracene	0.072–3.60	0.859	1.288	0.986	7%	0.032	0.097
Benzo[ghi]perylene	0.073–3.63	0.030	1.833	0.999	3%	0.000	0.001
Coronene	0.072–3.60	−0.065	1.175	0.996	7%	0.007	0.020
9H-Fluoren-9-one	0.362–18.1	−0.100	0.826	0.977	17%	0.090	0.269
9,10-Anthracenedione	0.280–14.0	−0.012	0.485	1.000	2%	0.001	0.002
1,8-Naphthalic anhydride	0.414–20.7	0.215	0.613	0.993	9%	0.115	0.34
Cyclopenta[def]phenanthrene	0.075–3.74	−0.058	0.479	0.987	17%	0.007	0.022
11H-Benzo[a]fluoren-11-one	0.081–4.06	0.016	0.157	0.988	12%	0.002	0.007
11 H-Benzo[b]fluoren-11-one	0.079–3.93	0.010	0.638	0.990	11%	0.007	0.022
Benzo[a]anthracene-7,12-dione	0.37–18.5	−0.704	3.026	0.995	9%	0.214	0.64

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Table 2a. Continued.

Analyte	Calibration range (ng)	<i>a</i>	<i>b</i>	R^2	Precision	LOD (ng)	LOQ (ng)
Malic acid	0.976–97.6	0.143	0.033	0.931	10%	0.377	1.132
Vanillin	0.057–5.67	−0.016	1.077	0.985	10%	0.006	0.018
Galactosan	0.221–22.1	0.046	1.288	0.992	11%	0.010	0.031
Mannosan	1.05–105	0.101	0.575	0.981	14%	0.261	0.78
Levoglucozan	3.42–342	0.405	0.495	0.994	6%	0.607	1.82
Phthalic acid	0.604–60.4	−0.003	0.239	0.983	14%	0.036	0.11
Vanillic acid methyl ester	0.054–5.44	−0.040	2.539	0.986	17%	0.007	0.022
Vanillic acid	0.054–5.38	0.016	1.170	0.987	13%	0.003	0.010
Syringic acid	0.053–5.34	−0.002	2.371	0.980	16%	0.010	0.030
Syringyl aldehyde	0.036–3.64	0.019	2.081	0.992	10%	0.001	0.004
Acetosyringone	0.036–3.64	0.019	2.081	0.992	10%	0.001	0.004
Syringylacetone	1.17–117	−0.050	2.951	0.996	9%	0.281	0.844
Retene	0.290–14.5	−0.217	1.871	0.997	7%	0.087	0.260
Isopimaric acid	0.142–14.2	0.043	0.155	0.997	12%	0.125	0.376
Dehydroabietic acid methyl ester	0.392–19.6	0.007	1.315	1.000	1%	0.001	0.004
Dehydroabietic acid	0.142–14.2	0.074	0.267	0.997	9%	0.117	0.351
Abietic acid	0.022–2.20	0.023	0.557	0.983	14%	0.005	0.014
7-Oxodehydroabietic acid	0.142–14.2	0.043	0.155	0.997	12%	0.125	0.376
Divanillyl	0.392–19.6	0.007	1.315	1.000	1%	0.001	0.004

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Table 2b. Validation parameters obtained from the calibration curves of SE-GC-TOFMS. Calibration range means lowest and highest standard concentrations used for the calibration curve; a = interception, b = slope (area ratio/mass ratio).

Analyte	Calibration range (ng)	a	b	R^2	Precision	LOD (ng)	LOQ (ng)
Phenanthrene	0.790–39.5	-0.048	1.190	1.000	2%	0.159	0.48
Anthracene	0.212–10.6	-0.353	1.542	0.991	10%	0.261	0.782
Fluoranthene	0.283–14.1	-0.112	1.384	0.996	6%	0.117	0.352
Pyrene	0.392–19.6	0.003	1.345	0.997	6%	0.067	0.202
Benzo[a]anthracene	0.290–14.5	0.107	1.461	0.995	8%	0.132	0.40
Chrysene	0.277–13.8	-0.002	0.549	0.998	5%	0.024	0.073
sum Benzofluoranthenes	0.098–4.89	-0.070	0.778	0.995	7%	0.011	0.033
Benzo[e]pyrene	0.134–6.71	-0.147	1.601	0.994	7%	0.037	0.110
Benzo[a]pyrene	0.130–6.49	-0.082	1.359	0.991	8%	0.078	0.234
Perylene	0.070–3.52	-0.135	1.313	0.984	12%	0.024	0.072
Indeno[1,2,3-cd]pyrene	0.069–3.44	-0.051	0.793	0.998	6%	0.002	0.007
Dibenzo[ah]anthracene	0.072–3.60	-0.099	1.394	0.948	14%	0.227	0.682
Benzo[ghi]perylene	0.073–3.63	-0.058	1.952	0.998	5%	0.005	0.014
Coronene	0.072–3.60	-0.323	1.298	0.996	6%	0.016	0.047
9H-Fluoren-9-one	0.362–18.1	-0.058	0.524	0.998	5%	0.011	0.032
9,10-Anthracenedione	0.280–14.0	-0.100	0.548	0.997	6%	0.018	0.053
1,8-Naphthalic anhydride	0.414–20.7	-1.115	0.327	0.969	9%	0.381	1.14
Cyclopenta(def)phenanthrenone	0.075–3.74	-0.123	0.932	0.985	15%	0.022	0.065
11H-Benzo[a]fluoren-11-one	0.081–4.06	-0.018	0.204	0.987	13%	0.005	0.015
11H-Benzo[b]fluoren-11-one	0.079–3.93	-0.045	0.580	0.982	18%	0.014	0.043
Benzo[a]anthracene-7,12-dione	0.37–18.5	-0.866	2.631	0.991	9%	0.428	1.28

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Table 2b. Continued.

Analyte	Calibration range (ng)	<i>a</i>	<i>b</i>	R^2	Precision	LOD (ng)	LOQ (ng)
Malic acid	0.976–97.6	-0.033	0.228	0.995	10%	0.098	0.293
Vanillin	0.057–5.67	0.004	1.353	0.999	4%	0.000	0.001
Galactosan	0.221–22.1	-0.054	5.112	0.990	14%	0.043	0.130
Mannosan	1.05–105	-0.009	1.200	0.996	9%	0.066	0.198
Levoglucozan	3.42–342	-0.003	0.558	0.999	4%	0.100	0.301
Phthalic acid	0.604–60.4	-0.014	0.376	0.994	12%	0.015	0.045
Vanillic acid methyl ester	0.054–5.44	-0.035	8.223	0.998	6%	0.003	0.008
Vanillic acid	0.054–5.38	0.005	4.595	0.998	4%	0.002	0.006
Syringic acid	0.053–5.34	-0.028	3.504	0.998	6%	0.002	0.005
Syringyl aldehyde	0.036–3.64	-0.001	3.941	0.989	9%	0.006	0.019
Acetosyringone	0.036–3.64	-0.001	3.941	0.989	9%	0.006	0.019
Syringylacetone	1.17–117	-0.018	0.307	0.995	10%	0.035	0.104
Retene	0.290–14.5	-0.653	2.035	0.982	19%	0.686	2.06
Isopimaric acid	0.142–14.2	0.058	0.237	0.996	6%	0.026	0.078
Dehydroabietic acid methyl ester	0.392–19.6	-0.047	1.432	1.000	3%	0.013	0.038
Dehydroabietic acid	0.392–19.6	0.003	1.345	0.997	6%	0.067	0.202
Abietic acid	0.022–2.20	0.007	0.563	0.938	9%	0.003	0.008
7-Oxodehydroabietic acid	0.142–14.2	-0.047	1.615	0.994	10%	0.019	0.056
Divanillyl	0.392–19.6	-0.035	8.223	0.998	6%	0.003	0.008

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Table 3. Concentration of PAH in NIST Standard Reference Material 1649a (Urban Dust).

Mean value mass of urban dust (μg)	SE-GC-MS		DTD-GC-MS		IDTD-GC-MS		Certified Values	
	14.8		62.5		46.3		Mean conc.	Confidence (95 %)
	Mean conc.	SD	Mean conc.	SD	Mean conc.	SD		
	$(\text{pg } \mu\text{g}^{-1})$		$(\text{pg } \mu\text{g}^{-1})$		$(\text{pg } \mu\text{g}^{-1})$		$(\text{pg } \mu\text{g}^{-1})$	
Phenanthrene	4.52	0.52	5.10	0.64	5.36	0.53	4.14	0.37
Anthracene	0.53	0.04	1.99	0.40	0.98	0.17	0.43	0.08
Fluoranthene	6.21	0.33	6.19	1.24	6.07	0.93	6.45	0.18
Pyrene	5.32	0.26	5.47	0.99	5.15	0.81	5.29	0.25
Benzo[a]anthracene	1.97	0.32	2.21	0.50	1.93	0.25	2.21	0.07
Chrysene	4.70	0.53	4.47	0.40	4.28	0.69	4.41	0.08
Benzo[b]fluoranthene	8.65	0.62	12.51 ^a	1.12	11.71 ^a	1.18	6.45	0.64
Benzo[k]fluoranthene	2.16	0.13					1.93	0.03
Benzo[e]pyrene	3.07	0.25	3.35	0.57	2.83	0.75	3.09	0.19
Benzo[a]pyrene	2.16	0.29	3.51	0.61	2.60	0.41	2.51	0.09
Perylene	0.68	0.11	1.27	0.53	0.44	0.10	0.65	0.08
Indeno[1,2,3-cd]pyrene	2.73	0.31	3.11	0.52	2.87	0.77	3.18	0.72
Dibenzo[a,h]anthracene	0.62	0.09	^b		0.88	0.23	0.29	0.02
Benzo[g,h,i]perylene	4.11	0.28	3.79	0.28	3.95	0.47	4.01	0.91

^a Sum of benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene.

^b Not quantified.

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Table 4. Concentration of levoglucosan, mannosan and galactosan in NIST Standard Reference Material 1649a (Urban Dust). A comparison with other publications.

Method	<i>n</i>	Levoglucosan		Mannosan		Galactosan		
		Mean conc. ($\mu\text{g } \mu\text{g}^{-1}$)	SD	Mean conc. ($\mu\text{g } \mu\text{g}^{-1}$)	SD	Mean conc. ($\mu\text{g } \mu\text{g}^{-1}$)	SD	
This study	IDTD-GC-TOF MS	3	165	1.4	20.5	1.0	10.8	1.8
Larsen et al. (2006)	PFE ^a GC-MS	3	162	8	–	–	–	–
Louchouart et al. (2009)	PFE ^b GC-MS	4	160.5	4.7	17.3	1.0	5.0	0.3
Kuo et al. (2008)	PFE ^b GC-MS	11	163.9	11.8	–	–	–	–

^a Pressurized fluid extraction with ethyl acetate, derivatization with BSTFA/TMCS, derivatization with BSTFA/TMCS (99/1, v/v) (Larsen et al., 2006).

^b Pressurized fluid extraction with CH₂Cl₂/CH₃OH (9/1, v/v), derivatization with BSTFA/TMCS (99/1, v/v) (Kuo et al., 2008).

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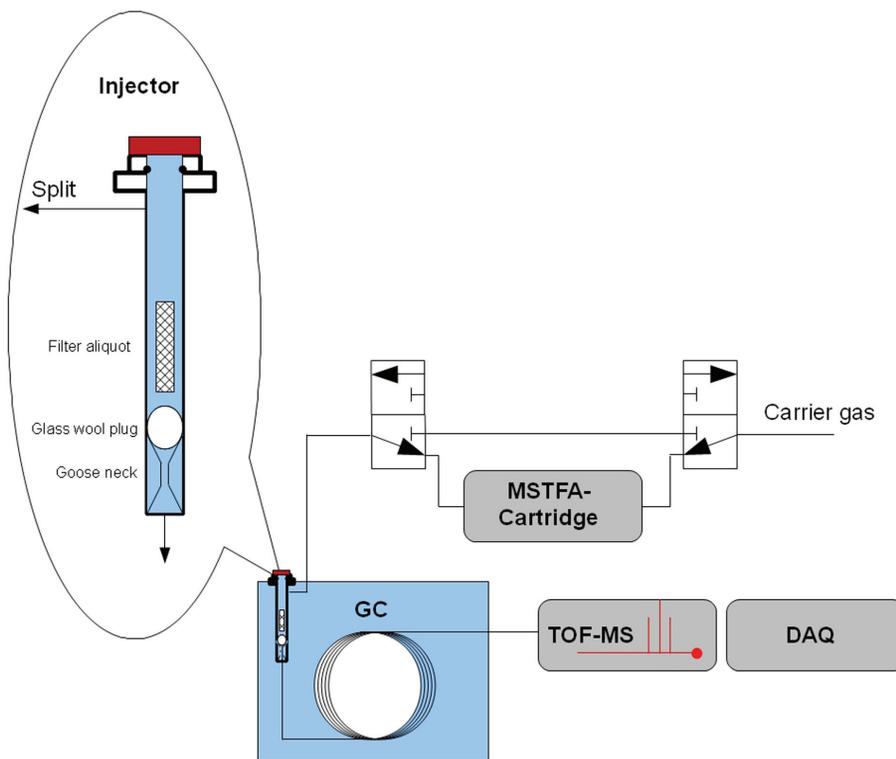


Fig. 1. In-situ derivatization and thermal desorption unit.

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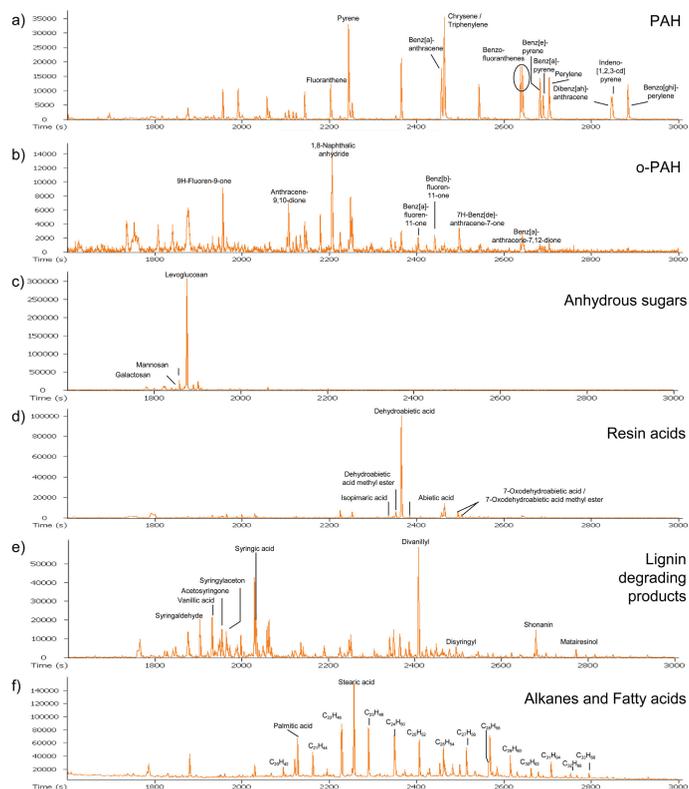


Fig. 2. Multiple ion chromatograms reflecting different groups of polar and non-polar analytes from a sample collected at the chemical characterization site at the UAS (urban background): **(a)** polycyclic aromatic hydrocarbons (PAH) (m/z 178 + 202 + 228 + 252 + 276 + 278), **(b)** oxidized PAH (o-PAH) (m/z 126 + 158 + 180 + 196 + 230 + 258), **(c)** anhydrous sugars (m/z 204 + 217), **(d)** resin acids (m/z 239 + 241 + 253), **(e)** lignin degradation products (m/z 194 + 209 + 224 + 238 + 279 + 297 + 327), **(f)** alkanes and fatty acids (m/z 57 + 117).

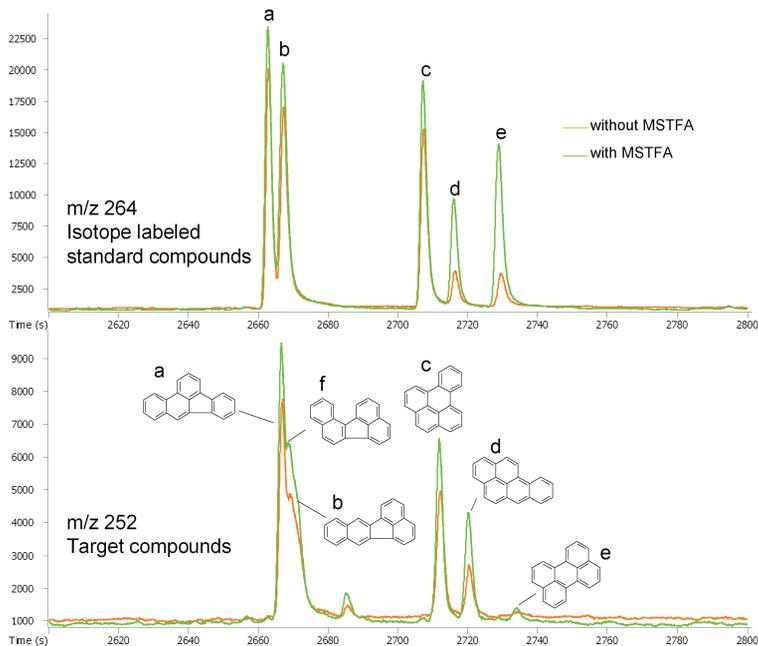


Fig. 3. The effect of filter matrix and MSTFA on sensitivity of PAH analysis. Orange line: 108 mm² filter of sampled PM₁ (equivalent to 200 l aerosol) analysed without MSTFA. Green line: 108 mm² filter of sampled PM₁ (equivalent to 200 l aerosol) analysed with MSTFA-saturated carrier gas during thermal desorption. The mass trace *m/z* 264 is shown for the isotope-labelled internal standards of **(a)** benzo[*b*]fluoranthene (0.802 ng), **(b)** benzo[*k*]fluoranthene (1.04 ng), **(c)** benzo[*e*]pyrene (0.802 ng), **(d)** benzo[*a*]pyrene (1.04 ng), **(e)** perylene (1.12 ng). Below the mass trace *m/z* 252 is shown for the corresponding native compounds with the exception that **(a)** benzo[*b*]-, **(f)** benzo[*j*]- and **(b)** benzo[*k*]fluoranthene could not be separated.

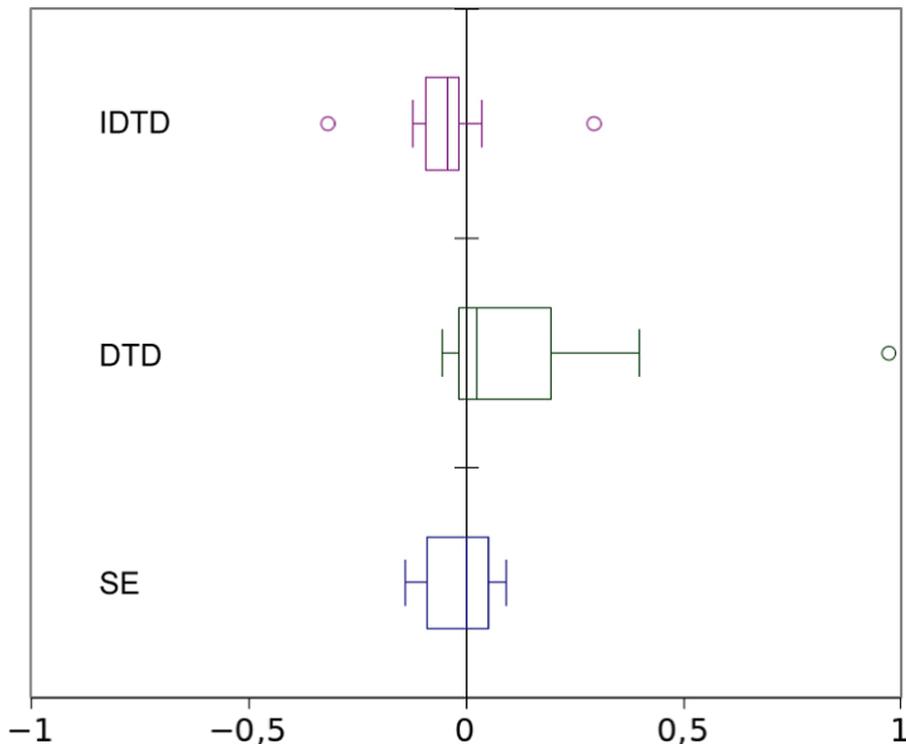


Fig. 4. Box plots for visualization of variations of the different methods applied to Standard Reference Material Urban Dust 1649a. The zero point on the scale refers to the certified values normalized to zero. Variations are calculated relative to the normalized certified values (1 = 100%). The extreme outliers of the results of anthracene and dibenzo[ah]anthracene are not visualized.

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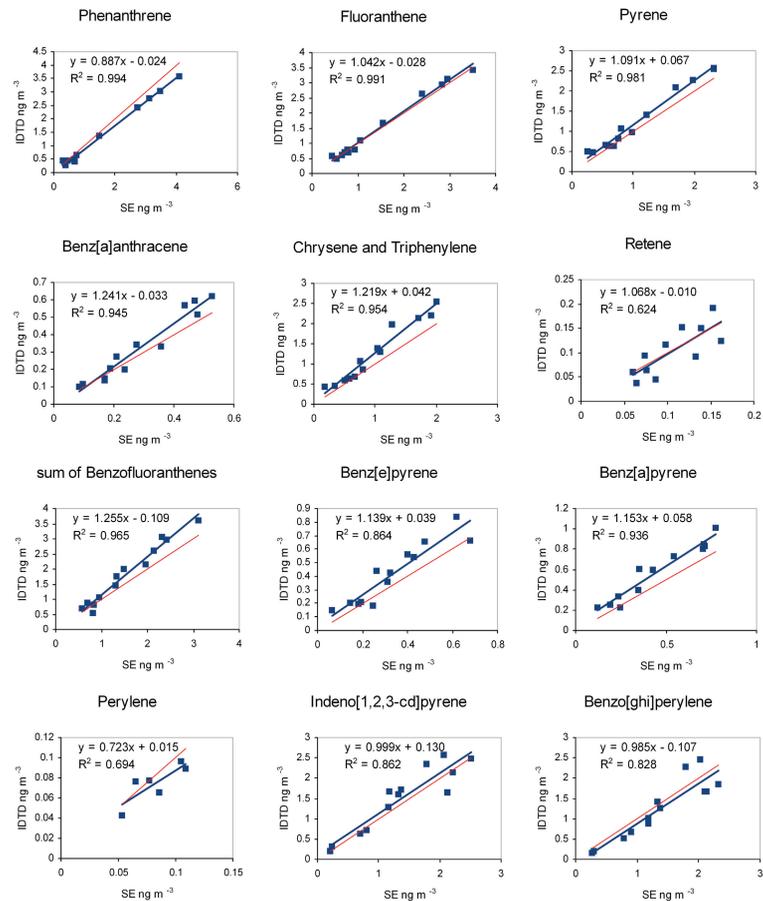


Fig. 5a. Correlation of IDTD and SE for analysis of PAH in ambient aerosol samples (blue: linear regression, red: line through origin, slope 1).

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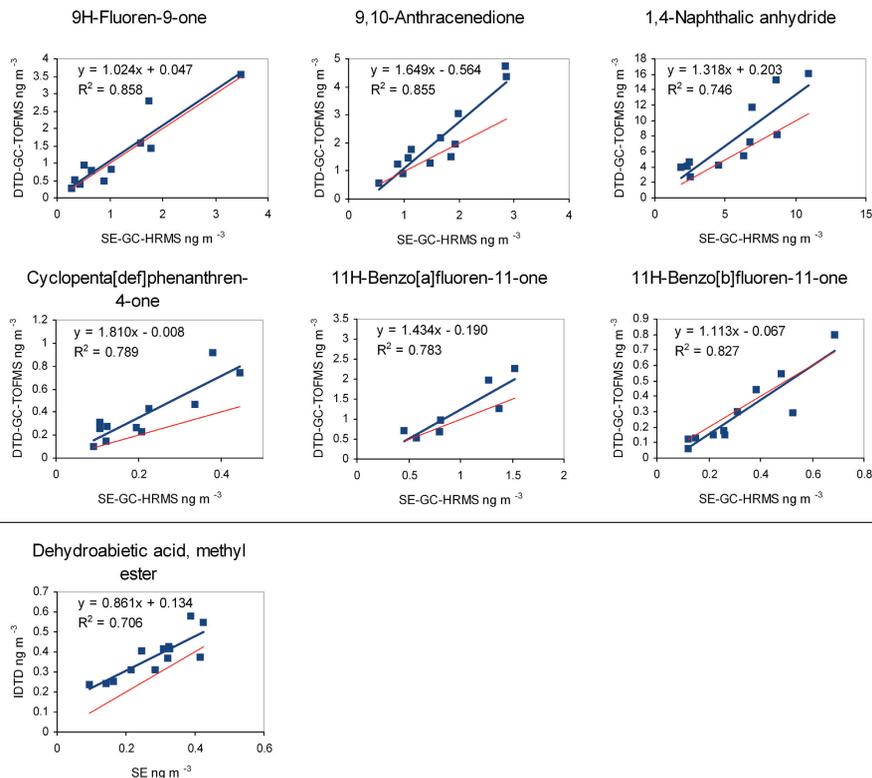


Fig. 5b. Correlation of IDTD and SE for analysis of o-PAH and dehydroabietic acid methyl ester in ambient aerosol samples (blue: linear regression, red: line through origin, slope 1).

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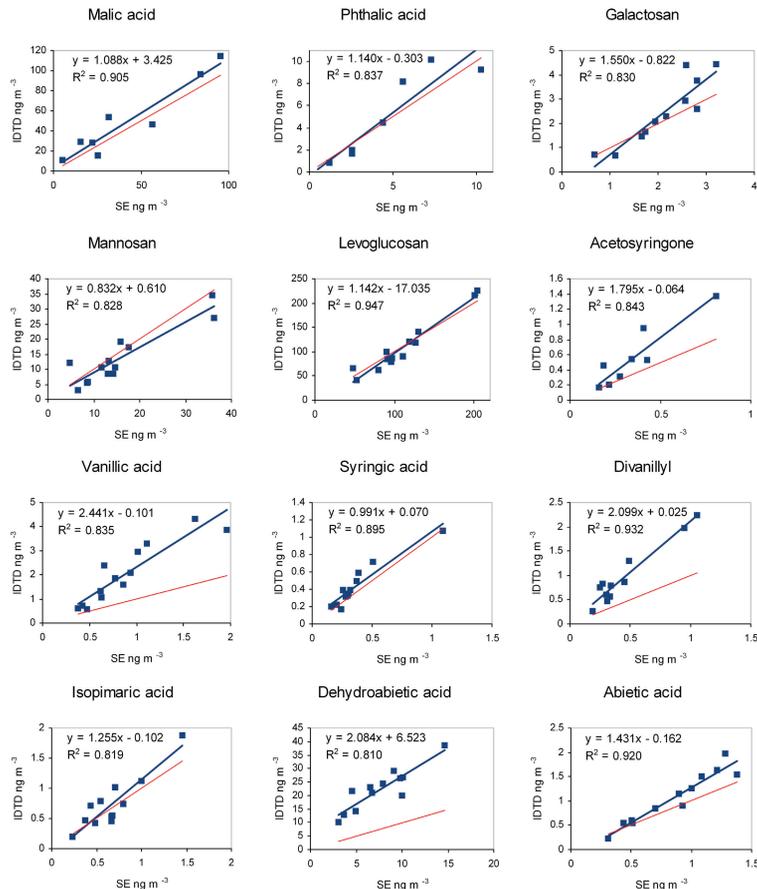


Fig. 5c. Correlation of IDTD and SE for analysis of polar substances in ambient aerosol samples (blue: linear regression, red: line through origin, slope 1).