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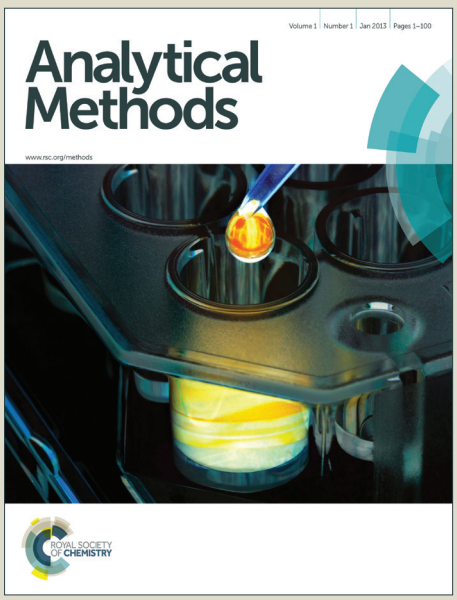

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Derivatization and analysis of levoglucosan and PAHs in ambient air particulate matter by moderate temperature thermal desorption coupled with GS/MS

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Author Contributions

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Abstract

A thermal desorption method followed by GC/MS analysis has been developed for efficient analysis of levoglucosan in particulate matter. The method requires the sample derivatization using N,O-bis(trimethylsilyl) trifluoroacetamide with 1% of trimethylchlorosilane. The reaction is carried out directly in the liner of a commercial thermo-desorption system on 2.1 mm $PM_{2.5}$ filter cuts under optimised conditions of temperature, 20°C, and reaction time, 5 minutes. A low temperature of 150°C is used for desorption, minimizing possible artefacts formation and allowing simultaneous detection of PAHs. The method is evaluated on standard reference material NIST 1649a and applied on ambient air samples. For a sampled air volume of circa 200 L, the overall analytical expanded uncertainty (OEU) for levoglucosan at concentrations of 500 ng/m^3 is around 25 %, while its detection limit (LOD) is circa 50 ng/m^3. In the case of benzo[a]pyrene, OEU at 1 ng/m^3 is 20 % and its LOD 95 pg/m^3.

Keywords: Levoglucosan, Thermo desorption, PM, PAH, Source Apportionment

1. Introduction

Levoglucosan (1,6-anydro-β-D-glucopyranose), together with minor quantities of its isomers such as mannosan, galactosan and 6-anydro-β-D-glucofuranose, is a product of cellulose pyrolysis at temperature higher than 300°C [1–4]. This compound is emitted in high quantities from biomass during uncontrolled burning conditions[5] and can travel long distances from the source due to its relatively high stability in the atmosphere[6]. As a consequence, it can be found in many

different environmental samples such as ambient air particulate matter (PM)[5,7], soil[8], sediments[9], char[10]. Numerous studies have used levoglucosan to evaluate the transport, transformation, and fate of atmospheric species. Beside levoglucosan, other organic compounds are usually monitored in PM adding useful information to assess emission sources by correlation analyses[6,11–15] or in source apportionment model studies[16–19]. Among these, PAHs profiles and diagnostic ratios have been largely used[16,19,20]. These approaches require accurate, detailed and high-time resolved datasets to examine relative concentrations and obtain significant predictive results, which is compatible with fast analytical methods.

Secondly, during the last years an increasing interest on levoglucosan has emerged due to its possible contribution to climate change. The hydroscopicity of levoglucosan affects the capacity of particles to absorb water[21] acting as condensation nuclei and influencing the scattering and absorption of solar radiation[22].

Levoglucosan is also important in other branches of chemistry, in particular the biofuel production from wood, in which levoglucosan acts as key intermediate agent[23,24].

The increasing importance of levoglucosan in the last years has driven researchers in exploring new analytical techniques for its fast and accurate analysis on aerosol particles. Many different analytical methods have been developed and subject for review[25].

The most popular methods for the analysis of levoglucosan are based on gas chromatography (GC) and mass spectrometry (MS) detection applied after extraction and eventual derivatization of the sample. Among the different extraction methods ultrasonic agitation was largely used[5,26,27], as well as Soxhlet[28] and pressurized fluid extraction[10,28,29]. Derivatization is usually introduced before GC-MS analysis increasing the analytes volatility and providing a better

chromatogram resolution and higher sensitivity. BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide)[5,10,28,29] and MSTFA (N-methyl-N-(trimethylsilyl) trifluoroacetamide) [26,28] with or without catalyzer were typical derivatization agents. Alternative methods were considering high-resolution liquid chromatography followed by mass spectrometry[8,30–33] or high-performance anion-exchange chromatography with pulsed amperometric detection[34–36]. All these methods require liquid extraction and are generally laborious. Moreover, many of these methods have not been validated, mainly due to the lack of an appropriate reference material for levoglucosan concentration in PM. In fact, the standard reference materials (SRM) 1649a, urban dust (National Institute of Standards & Technology, USA), contains a reference concentration for levoglucosan, not certified[28].

The use of thermal desorption for the direct extraction of analytes from particulate matter shows numerous advantages with respect to conventional solvent extraction: reduction of the sample preparation time, prevention of contamination due to the minimal use of glassware and reduction of analytes losses. This technique has been used for analysing semi volatile organic compounds[37–42] and for polar compounds determination[42,43] including levoglucosan[44,45]. The improvements brought by TD and chemical derivatization were recently combined for analysis of levoglucosan on $PM_{2.5}$ filters[45].

In this work we apply TD technique coupled with derivatization reaction on $PM_{2.5}$ filters followed by direct GC injection. The derivatization occurs in a single step, manually injecting the reagent on small diameter filters (2.1 mm) directly in the inlet liner of the desorption unit. Derivatization provides a single and well defined chromatographic peak, and the choice of the filter dimension allows balancing analytical noise with detection limits compatible with 24 h low volume sampling. TD is performed using a commercial thermo-desorption unit (TDU) mounted

on a cooled injection system (CIS). The desorption method developed, uses a low temperature of desorption in order to avoid the pyrolysis of cellulose possibly present on PM samples and eventual artefact formation. Using such desorption condition the method has been implemented to quantify in a single analysis levoglucosan and polycyclic aromatic hydrocarbons (PAH). .Analytes determinations obtained for Standard Reference material NIST 1649a are compared with previously reported values[10,28,29] and used to validate the method for contemporary analysis of PAHs. The method is finally employed for analysis of filters collected in a monitoring station for air quality located in remote area, demonstrating the application of the proposed technique for high-time resolved monitoring and source apportionment studies.

Experimental section

2.1 Ambient air $PM_{2.5}$ Sampling

$PM_{2.5}$ ambient air samples were collected on 47 mm (OD, Whatman®) quartz filters by a Low Volume Sampler (Derenda, Teltow, Germany) in a semirural background area close to the European Monitoring and Evaluation Programme (EMEP) station situated at the Joint Research Centre (JRC-Ispra, Italy). The samples were collected for 12 days between 13 and 29 October 2010, every 24 h at a flow rate of about 38 L min^{-1}. Contemporary filter sampling was performed for analysis of elemental carbon (EC) and organic carbon (OC) using a Sunset Dual-optical Lab Thermal-Optical Carbon Aerosol Analyzer and analysis protocol EUSAAR[46] (Repeatability Standard Deviation, RSD < 10%).

2.2 Solvent, standards and reagents

Levoglucosan (99%) was obtained from Sigma Aldrich (St. Louis, MO, USA). Levoglucosan deuterated (D7, 98%) was used as internal standard (CIL, Andover, MA, USA). We used N,O-bis(trimethylsilyl) trifluoroacetamide with 1% of trimethylchlorosilane (BSTFA+TMCS) as derivatizing agent (Sigma-Aldrich GmbH, USA). PAH standard solutions were obtained through dilutions of mother solutions MIX 45, from Dr. Ehrestorfer (GmbH, Augsburg, Germany) containing 18 compounds and addition of MIX 9D (Dr. Erhenstorfer), containing 16 of the corresponding deuterated PAHs. Table 1 reports a list of the analysed compounds and their acronym.

The solvents used were cyclohexane (CH) pesticide residue grade, dichloromethane (DCM) HPLC grade and acetonitrile(ACN) HPLC grade, all obtained from Sigma-Aldrich, USA.

Standard reference material 1649a, urban dust (National Institute of Standards & Technology, USA) was used to provide reference values.

2.3 Sample preparation for TDU injection: extraction and derivatization

Filter samples and calibration standard solutions were derivatized directly in the TDU liner. The liners were pre-cleaned and prepared with a plug of glass wool surmounted by a clean quartz filter as previously reported[47]. Sections of low volume air filters of 2.1 mm diameter were placed on top of the TDU filter and spiked with two internal standard solutions: the first standard solution consisted of 3 µL of levoglucosan deuterated at concentration of 11 ng/µL or 53 ng/µL; the second consisted of 1 µL of deuterated PAH mixture at 488 pg/µL. Finally, 5 µL of BSTFA+TMCS were imbibed onto the filter for a complete derivatization reaction. Calibration

standard solutions were injected on the clean quartz filter in the TDU liner before spiking with the internal standards. Injections which required a precise and accurate volume were performed using plunger-in-needle syringes (Hamilton Company, USA). The injections where performed after placing the TDU liners on a closed vial and through the cap septum.

SRM was firstly analyzed by a common method of liquid extraction, concentration, clean-up, derivatization and quantification[5,10,26–29]. In particular, the following procedure was used: About 5 mg of SRM were extracted for 30 min by ultrasonic agitation with 6 mL of ACN:DCM (50:50) mixture in a closed vial. To avoid the complete evaporation of the extract solution prior to derivatization, ACN was used as a polar solvent instead of methanol or acetone. Then 8 µL of a standard solution at 53 ng/µL of deuterated levoglucosan was added as internal standard before extraction. After extraction, the sample was filtered; evaporated to circa 300 µL and then 50 µL of BSTFA were added for derivatization reaction at 40°C for 15 minutes. An aliquot of 50 µL was deposited on the TDU liner prepared with a plug of glass wool surmounted by a clean quartz filter for analysis.

In addition, the SRM was also analyzed by re-suspension and deposition of the material on a small section of quartz filter adapted to the TDU liner for thermo desorption analysis. This procedure was used to mimic PM collected on real filter samples. The sample was prepared in a small vial by dissolving quantities between 1 and 2 mg of SRM in 400 µL of ACN:DCM (50:50) mixture, adding 20 µL of deuterated levoglucosan at concentration of 53 ng/µL, 3 µL of deuterated PAH mixture. Subsequently, 100 µL of BSTFA+TMCS were added for derivatization. The mixture was agitated and 50 µL of suspension were deposited on the TDU liner filter. These samples were also used for optimization of the reaction parameters (see Method Development Section).

2.4 Analysis

All the analyses were performed by means of a gas chromatographer (GC 6890, Agilent Technologies, USA) coupled with a mass spectrometer (MS 5975C inert, Agilent Technologies, USA) equipped with a thermal desorption injection system (TDU/CIS4, Gerstel, GmbH). The desorption system consists of a high volume thermal desorption unit (TDU) with a exchangeable liner directly connected to a cold trap injector system (CIS) for focalization and controlled injection into the column of the gas chromatographer. Detailed description of the system can be found elsewhere[37]. The injection conditions were as follow: TDU initial temperature of 30°C and solvent venting injection mode kept for 30 seconds; subsequent fast TDU ramp (720°C/min) to the final desorption temperature (tested at 120, 150, 170, 200 or 300°C) and a hold time of 10 minutes; transfer line temperature equal to TDU desorption temperature; cryogenic trap (CIS) hold at -15°C during thermo desorption and subsequent ramp to a final temperature (tested at 250, 340 and 400°C); flow parameters set as previously reported[37,47].

The chromatographic separation was performed using a capillary column Rxi®-5Sil MS (30 m, i.d. 0.25 mm, phase thickness 0.25 μm). The GC oven was temperature programmed as follows: initial temperature 40°C, hold for 5 min; first ramp of 6°C/min to a final temperature of 230°C, hold for 3 min; second ramp performed at the rate of 30°C/min to 320°C, hold for 4 min. This ramp provided good separation of levoglucosan and the 14 PAHs selected for quantification (Figure S1).

Blanks of the system were performed each day before the sample sequence to eliminate possible contamination from the desorption system. Moreover, fast blank analysis with final desorption

temperature of 340°C were preformed between samples to eliminate possible carry over from the desorption system and the column.

2.5 Calibration

Internal standard technique was used for calibration, on the basis of the ratios [Area Analyte/Area Deuterated Internal Standard] versus the ratios [Concentration Analyte/Concentration Deuterated Internal Standard] for levoglucosan and for the corresponding analyzed PAH. Calibration standard solutions at four different concentration ratios were prepared under repeatability conditions to test linearity (R^2 reported in Table S2).

2. Results and discussion

3.1 Method development – derivatization conditions

Time and temperature of reaction were optimized on calibration standards. 1 µl of standard solution was placed on the liner filter followed by 5 µL of BSTFA+TMCS and 5 µL of ACN for a better contact between derivatizing agent and standard. The liner was kept on a capped 8 mL amber vial for the reaction times of 5, 15, 30 and 45 minutes at temperature of 60˚C (n = 3), and for 5 minutes at temperature of 20°C (± 2°C) (n = 2). No significant differences among temperatures and times were found for levoglucosan and its internal standard, both in terms of absolute or relative response (Figure 1). As a consequence, reaction temperature of 20°C and reaction time of 5 minutes were used for sample analyses. These conditions allowed performing the derivatization reaction while the instrument was preparing for injection and, together with the elimination of solvent extraction steps, provided a reduction of the overall analytical time (Figure 2).

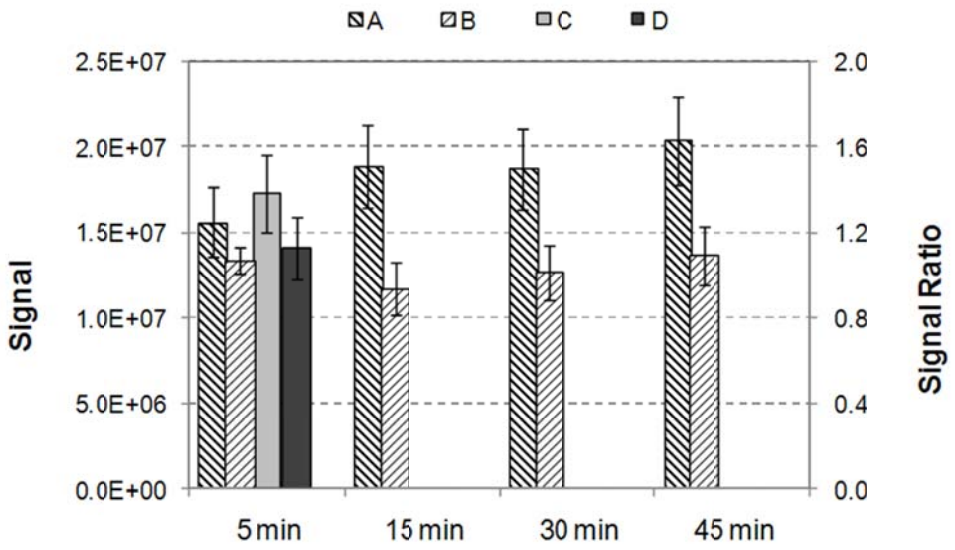

Figure 1. Optimization of derivatization parameters (time and temperature): A = Signal (area) at 60°C; B = Signal Ratio at 60°C; C = Signal at 20°C; D = Signal Ratio at 20°C.

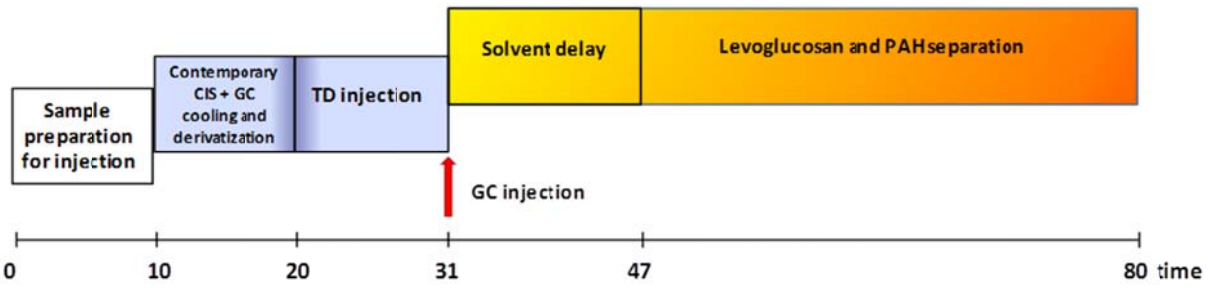

Figure 2 – Scheme of the analytical steps and overall analytical time per single sample.

3.2 Method development –thermo desorption conditions

The best temperature conditions for TD injection were tested on SRM to work on a matrix similar to real samples. Replicated extractions of SRM were performed using both ACN and ACN:DCM. Moreover, SRM was analysed after re-suspension and deposition on quartz filter section.

The optimisation of CIS and TDU desorption temperatures for PAH analysis was object of a previous publication[37]. To evaluate possible temperature effects on levoglucosan response desorption temperature was tested on SRM, on the base of the previous results. CIS injection temperatures were tested at 400°C (maximum recommended temperature), 340°C and 250°C. Replicated analyses showed no influence in levoglucosan response and calculated concentration. On the other hand, the response of higher molecular weight PAHs (i.e, up to B[ghi]P) was strongly decreasing with the decrease of the CIS injection temperature, in particular from 340 to 250°C. Consequently, CIS temperature was kept at 340°C to preserve the column and allow for complete desorption of all the analysed PAHs and prevent memory effect.

TDU desorption temperature was tested at 200°C and 300°C for analysis of liquid extracts. Paired t-tests showed no significant differences at 95 % confidence level for the analytical results of the liquid extracts, providing concentration levels of levoglucosan of 85 ± 11 mg/kg (n=6). Such a value was in agreement with the concentration reported on the SRM 1649a certificate of analysis and to the concentration reported by Larsen et al.[28] (81 ± 9 mg/kg).

TDU desorption temperature was then tested at 120, 150, 170, 200 and 300°C on the suspended SRM matrix. In this case, a positive correlation between levoglucosan quantification and desorption temperature was shown. Levoglucosan concentrations resulted in 90 mg/kg at TDU

desorption temperature of 120°C, 78 ± 8 mg/kg (n=4) at 150°C, 95±2 mg/kg (n=2) at 170°C, 143±15 mg/kg (n=4) at 200°C and 1265±179 (n=2) at 300°C (Figure 3).

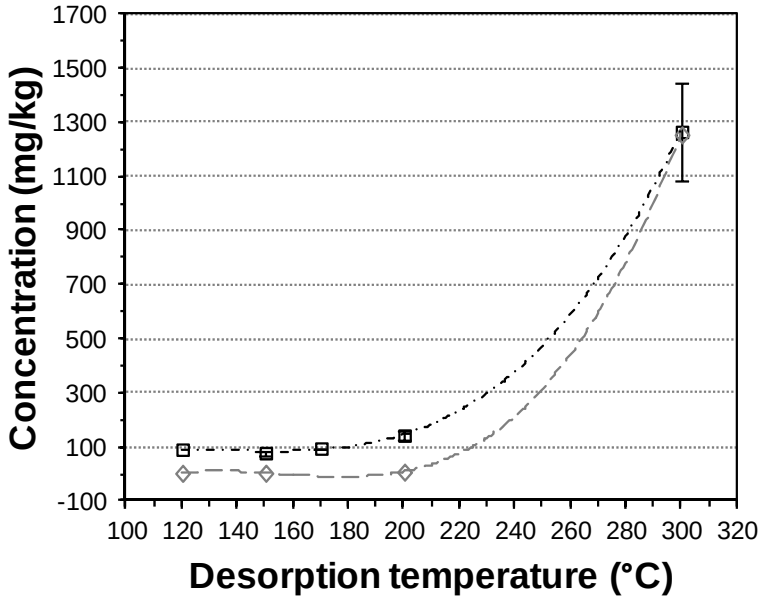

Figure 3. Levoglucosan concentrations detected in SRM ( ) and in cellulose ( ) analysis at different TDU desorption temperatures.

The exponential increase in levoglucosan concentration observed when temperatures rise over 200˚C could be due to artefacts generated from the cellulose present in the vegetable fraction of the air dust[48,49] during the thermal desorption phase at the TDU, occurring under nitrogen stream. In fact is well known that pyrolytic conditions at temperature higher than 300˚C promote levoglucosan formation from cellulose[1–3].

The hypothesis of levoglucosan formation as an artefact of cellulose was confirmed by the direct analysis of amounts of circa 0.8 mg of high purity cellulose powder (Aldrich) carried out at different temperatures by our thermal desorption system. A similar behaviour to the SRM was

shown by cellulose when changing desorption temperature: at desorption temperatures of 120, 150 and 200°C only traces of levoglucosan were reported (respectively 3.6, 3.9 and 7.9 mg/kg), while high levoglucosan concentrations were determined when desorption temperature was operating at 300°C (1254 mg/kg, Figure 3).

The levoglucosan concentrations found in both the analyses for the SRM extracts and the suspended SRM were in agreement with the reference concentration[28]. This value has been questioned by other authors[10,29], who found double amount in their samples. They explain this difference by a possible alteration of the specific SRM or by an analytical artefact. However, no clear conclusion can be made on the true value of the sample, and this issue still need to be addressed.

Since at TDU temperature lower than 170°C the analyses of both the suspended SRM and cellulose showed no significant differences amongst levoglucosan determinations, to minimize any possible artefact formation, a temperature of 150°C was chosen as operating desorption temperature at the TDU.

Regarding PAHs, the temperature of desorption had no effect on their calculated concentrations. On the other hand, it influenced the response of less volatile PAHs, which decreased with the decrease of the desorption temperature, as discussed in the following section. A good agreement between determined and certified concentrations was found for most of the analyzed PAHs: deviations with respect to the certified value were under 20 % except for Anth (+66 %), Chry+Tph (+ 33 %) and DB[a,h]A (+ 28 %), as they were close to detection limit (Figure 4).

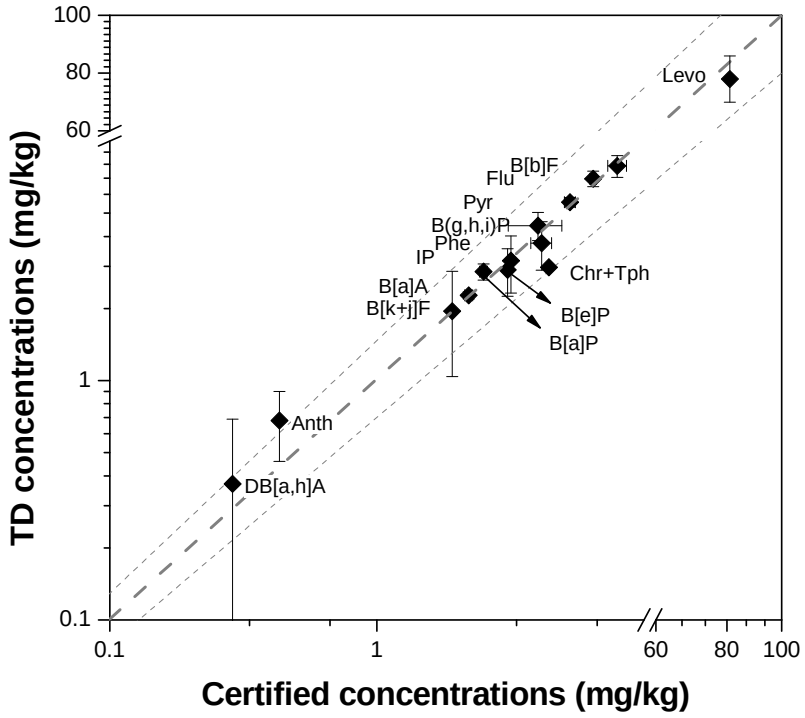

Figure 4. Comparison of PAH and levoglucosan thermo desorption (TD) determinations versus certified values in SRM 1649a. Dashed line (– – – –) represents ideal correlation; short dash lines (·····) represent ± 20% deviation. Expanded uncertainties (⊢—⊣) are reported at 95 % level of confidence.

3.3 Analytical uncertainty and detection limit for filter sample determinations

In general, the main sources of uncertainty in thermo desorption filter determinations analyses are related to: a) the certified reference standard; b) the preparation and dilution of calibration standards; c) the regression of the calibration curve; d) the internal standard injection; e) the filter

cutting; f) the efficiency of desorption. Moreover, in the case of levoglucosan analysis g) the deposition of the derivatizing agent and h) the derivatization reaction need to be considered.

Uncertainties associated with the reference material and the calibration standard preparation were estimated to range from 3.1 to 4.3 % depending on the compound and standard concentration. These uncertainties were considered as inputs in the evaluation of the uncertainties derived from the calibration curve. For calibration, the correlation between concentrations and response ratios with respect to the internal standards was considered. The output concentration ratios and associated uncertainties (u_{CL}) were estimated from orthogonal linear regression following ISO 6143[50]. The response ratios of the levoglucosan calibration line ranged from 0.17 to 5.7 while corresponding uncertainties decreased from 13 % to 8 %. With respect to the PAHs, the response ratios ranged from 0.02 to 2.07. The values of the corresponding uncertainties were depending on the compound. For B[a]P in particular, uncertainty was progressively decreasing from 31% to 5.6% with the increase of the response ratio (from 0.02 to 2.07). In general, the higher uncertainties were related to lower response ratios and to compounds with higher detection limits or separation problems such as Anth (28-5%), Chry+Tph (26-8%), B[b]F (36-10%), B[a]P (31-6%), DB[a,h]A (46-6%). Uncertainties lower than 10% were generally obtained for response ratios greater than 0.5. It is noted that the heaviest PAHs showed lower absolute responses (Figure S1) and higher uncertainties compared to lighter PAHs at the same concentration range. This was a consequence of the optimized desorption temperature (TDU desorption temperature =150˚C) used for levoglucosan determination.

The volumetric injection of the internal standard introduced a reproducibility uncertainty of circa 2.1 %, as tested in a previous study[37]. The uncertainty associated to the internal standard solution

preparation was estimated as 3.55% for the deuterated levoglucosan solution and 1.65% for the deuterated PAH solution. These combined uncertainties are indicated in the following as u_{IS}.

The reproducibility uncertainty (u_R) was calculated from replicates analysis of different filters. It included the uncertainties due to the cut of the filter, inhomogeneity of the sampled filter, the deposition of the sample and reagent in the liner, the efficiency of the derivatization reaction and of the thermal desorption. The uncertainty was estimated through the standard deviation of the analytical response of identical cut sections from the same filter. For levoglucosan the relative standard deviation (RSD, Table 2) of such replicate filters was decreasing from 26 % to 6 % in the concentration range 10 - 125 ng/filter, with an average value of circa 10 % for concentrations greater than 60 ng/filter. In the case of the PAHs, the RSDs were, generally lower than 25 % with few exceptions, i.e. compounds at a very low concentration (Anth, IP and B[e]P). The inter-compound average RSD was 13 ± 7 %.

On the basis of these considerations, an overall analytical uncertainty (*ou*) was calculated by combining the afore-mentioned uncertainties by means of the following equation:

$$ou = \sqrt{u_{CL}^2 + u_{IS}^2 + u_R^2}$$

Overall expanded uncertainties, OEU, were calculated at 95 % confidence level by multiplying *ou* by a factor of 2. Figure 5 represents OEU, for levoglucosan and B[a]P as well as the corresponding expanded uncertainties related to the calibration line u_{CL}, and the internal standard, u_{IS}.

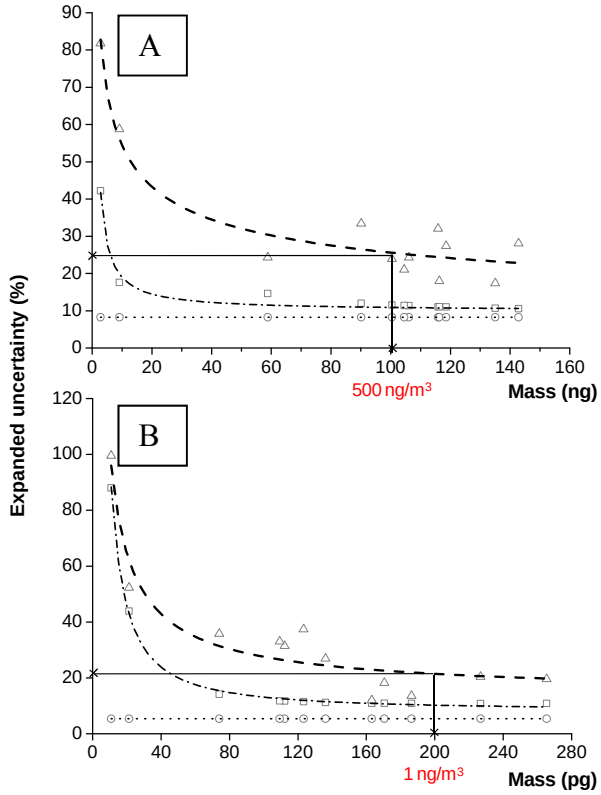

Figure 5. Expanded uncertainties calculated for levoglucosan (A) and B[a]P (B): associated to the calibration curve, eu_{CL} (-·-·-·-), to the internal standard, eu_{IS} (·····), and the overall expanded uncertainty, OEU (– – –).

For a levoglucosan concentration in low volume $PM_{2.5}$ filters of 500 ng/m^3, typical of a rural area such as the selected sampling site at the beginning of the winter[17,51], OEU of about 25% was found.

Regarding the PAHs a general increase in the OEU values was observed with respect to similar thermal desorption analyses [37], which did not include any derivatization step and were carried out on 5.45 mm diameter filters. For a B[a]P concentration of 1 ng/m^3, the OEU increased more

than twice (OEU = about 20 % in respect to the previously reported value of 8 %). This increase is explained by the additional manipulation of the sample, the more complex analytical matrix, the smaller filter dimensions and the lower operational temperature of desorption. The reported repeatability values are comparable to results obtained for classical liquid extraction method, with the advantage of TD reduction of sample preparation time.

Limits of detection and quantification (LOD and LOQ) were calculated as 3 and 10 times the u_{CL} of blank samples from filters of 12.9 mm diameter.

In the case of levoglucosan LOD and LOQ were respectively 10 ng and 34 ng, while in the case of B[a]P they were respectively 19 pg and 65 pg, in accordance with previously reported data. The values are expressed in terms of amounts injected into the analytical instrument. Considering that the presented method was validated on a 39 mm filters sampled with a volume of about 50 m^3 of air, from which a sample volume of about 0.19 m^3 was analysed (for a 2.1 mm diameter filter section), the detection limit in air would be about 51 ng/m^3 for levoglucosan and 98 pg/m^3 for B[a]P. As levoglucosan levels measured in rural and urban aerosol in winter time are typically in the range of 200–2000 ng/m^3 [15,35,36,52], the method results sensitive enough for this purpose. Nevertheless, detection limits expressed in air concentration can be decreased by increasing the section diameter of the filter analysed (Table S3 shows the equivalent sampling volume for different considered filter sections). So, in case of lower filter concentrations, as can be registered during summer time or in remote areas, a bigger filter sections (5.45 mm diameter) would be necessary [37] for resulting in detection limit of about 8.9 ng/m^3. The sensitivity of the method when sampling 50 m^3 on low volume 47 mm diameter filters is in accordance with other values reported in the literature[26,35,52].

3.4 Determinations on $PM_{2.5}$ filter samples from a semirural background area

Results of levoglucosan and PAH replicate analyses of the twelve LVS filters are reported in Table 2 as ng/m^3 and Table S1 in terms of quantified mass. Table 2 also reports values of filter contents for the contemporary measures of EC, OC, temperature, relative humidity and sample volume. Levoglucosan concentrations were comprised between 85 and 719 ng/m^3 (10 – 154 ng injected), while those of B[a]P were comprised between 139 and 1401 pg/m^3 (19 – 300 pg injected). These concentrations are in line with previously reported values for this sampling site[17,19]. In the supporting material, details for the trends (Figure S2), correlations (Figure S3) of levoglucosan and the sum of the heavier PAHs with other emission sources parameters are reported and discussed. The reported data support findings from previous source apportionment studies[17,19], which indicate wood combustion as a main contribution to carbonaceous aerosol and PAHs emission in the Ispra site.

3. Conclusions

The present method is based on the derivatization of levoglucosan on small $PM_{2.5}$ filter cuts, which are placed inside a thermo-desorption unit followed by a cooled injection system, providing a focalized injection inside the GC column. This operational mode eliminates solvent extraction and clean up preparation steps, reducing the analytical time required for analysis of a liquid sample. For detection of levoglucosan and PAHs from Phe to B[ghi]P, the overall time of sample preparation can be reduced to 15 minutes (including the preparation of the sample in the liner and the injections of the internal standards and derivatization agent), i.e. by a factor of 4 to 240 times, when compared to other extraction and derivatization methods (Figure 2).

Furthermore, the elimination of solvent extraction reduces the analytical costs and environmental impacts. As derivatization is performed directly on the filter placed inside the desorption liner, analyte losses are minimized. Moreover, since derivatization is separated from the instrumental analysis, the method can be applied on any TD system of similar characteristics. The operational conditions have been optimized to prevent the formation of artefacts during desorption, still being possible the simultaneous analysis of PAHs with acceptable associated uncertainties under ± 25 % for typical ambient air concentrations.

In practice, the developed methodology would allow for levoglucosan limits of detection in ambient air concentration of circa 1. 83 ng/m^3 for 24 h sampling or 44 ng/m^3 for 1 h sampling by analysing a filter section of 12.9 mm diameter, i.e. a sample volume of 5.47 m^3. Under the same conditions, B[a]P limit of detection is about 1.63 pg/m^3 for 24 h sampling and 39 pg/ m^3 for 1 h of sampling. These limits of detection allow hourly-based monitoring of levoglucosan and PAHs in ambient air for more comprehensive source apportionment studies.

Supporting Information

Additional material includes masses quantified in ambient air filter samples and relative standard deviations, a standard GC-MS chromatogram and discussion of emission trends and correlations.

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Table 1 – List of analysed compounds, their corresponding acronyms, retention times (RT) and quantification ion (QI).

Compounds	Acronym	QI	RT (min)
Levoglucosan	Levo	217	27.348
Phenanthrene	Phe	178	28.84
Anthracene	Anth	178	29.049
Fluoranthene	Flu	202	33.435
Pyrene	Pyr	202	34.242
Benzo[a]anthracene	B[a]A	228	39.458
*Chrysene+Triphenylene	Chry+Tph	228	39.656
Benzo[b]fluoranthene	B[b]F	252	42.285
*Benzo[k+j]fluoranthene	B[k+j]F	252	42.314
Benzo[e]pyrene	B[e]P	252	42.650
Benzo[a]pyrene	B[a]P	252	42.721
Perylene	Per	252	42.824
Indeno[1,2,3,-c,d]pyrene	IP	276	44.137
Dibenzo[a,h]anthracene	DB[a,h]A	278	44.170
Benzo[g,h,i]perylene	B[g,h,i]P	276	44.482

* Sum of the co-eluting isomers

Table 2 – Average concentrations of levoglucosan (ng/m^3), PAHs (pg/m^3), EC (µg/m^3), OC (µg/m^3) found in ambient air filters at Ispra site and their respective standard deviations (SD). Sampling temperature (T), relative humidity (RH) and volume (V) are also reported.

Acronym	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5		Filter 6		Filter 7		Filter 8		Filter 9		Filter 10		Filter 11		Filter 12	
	Average	SD n=6	Average	SD n=8	Average	SD n=4	Average	SD n=4	Average	SD n=3	Average	SD n=4	Average	SD	Average	SD n=3	Average	SD n=4	Average	SD n=3	Average	SD n=3	Average	SD n=4
Levo	507	50	393	101	534	54	305	28	457	68	85	20	582	83	527	43	584	37	595	70	675	40	719	91
Phe	1.18	0.15	7.17	1.28	1.05	0.12	1.27	0.28	1.57	0.25	1.32	0.26	0.78	0.21	0.91	0.04	0.81	0.16	0.77	0.03	0.69	0.12	0.81	0.003
Anth	<DL		<DL		0.22	0	0.25	0	<DL		<DL		<DL		0.24	0.03	0.23	0.03	<DL		<DL		0.22	0.01
Flu	0.48	0.07	3.4	0.39	0.64	0.02	0.5	0.03	0.53	0.06	0.41	0.07	0.53	0.08	0.5	0.05	0.59	0.05	0.64	0.07	0.6	0.07	0.65	0.11
Pyr	0.44	0.08	2.54	0.31	0.59	0.02	0.52	0.05	0.55	0.02	0.35	0.06	0.59	0.11	0.49	0.06	0.58	0.06	0.66	0.11	0.58	0.05	0.64	0.13
B[a]A	0.23	0.04	1.01	0.18	0.25	0.06	0.24	0.04	0.25	0.06	0.14	0.02	0.33	0.07	0.25	0.01	0.35	0.02	0.42	0.05	0.5	0.09	0.46	0.04
Chry+Tph	0.31	0.04	0.86	0.13	0.32	0.04	0.34	0.04	0.37	0.03	0.14	0	0.5	0.07	0.35	0.05	0.48	0.02	0.61	0.06	0.66	0.09	0.7	0.01
B[k+j]F	1.25	0.3	1.43	0.22	1.4	0.14	0.66	0.06	1.77	0.02	0.25	0.05	1.28	0.23	1.38	0.19	1.7	0.01	2.17	0.2	2.03	0	2.38	0.
B[b]F	0.38	0	<DL		0.41	0.08	0.32	0.08	0.5	0.03	<DL		0.55	0.07	0.35	0.05	0.46	0.06	0.54	0.09	0.65	0.09	0.48	0.
B[e]P	0.53	0	<DL		0.57	0.17	0.39	0.09	0.71	0.04	0.11	0.01	0.83	0.01	0.57	0.15	0.91	0.14	1.07	0.14	1.25	0.2	1.23	0.19
B[a]P	0.67	0.1	0.65	0.12	0.65	0.1	0.45	0.07	0.81	0.1	0.14	0.02	0.96	0.02	0.73	0.13	1.1	0.04	1.01	0.07	1.24	0.05	1.54	0.14
Per	0.11	0.02	<DL		0.11	0.01	0.08	0	0.15	0.02	<DL		0.15	0.01	0.09	0.02	0.17	0.01	0.18	0.02	0.20	0.03	0.24	0.02
IP	0.55	0	0.61	0	0.93	0	0.23	0	0.61	0	0.12	0.	0.97	0.	0.6	0	0.83	0	0.88	0	1.15	0	1.16	0.
DB[a,h]A	0.12	0	<DL		0.22	0.03	0.1	0.01	0.12	0.02	<DL		0.2	0.05	0.14	0.02	0.17	0.02	0.19	0	0.26	0.05	0.26	0.05
B[ghi]P	0.6	0.04	0.48	0.11	0.45	0	0.24	0.01	0.58	0.02	0.13	0.01	0.87	0.08	0.53	0.01	0.76	0.1	0.85	0.1	1.17	0.1	1.12	0.15
EC	2.44		2.58		3.27		1.55		2.10		0.47		2.18		2.18		2.13		2.68		3.09		3.19	
OC	10.9		10.2		13.1		3.5		6.1		1.3		8.7		10.8		6.1		8.7		10.6		12.0	
T (°C)	4		4		4		1		-1		2		0		0		-2		-2		-2		0	
RH (%)	70		74		71		64		63		47		64		71		73		68		68		76	
V (m^3)	55.31		6.77		55.31		55.32		55.31		55.30		55.31		55.31		55.32		55.31		55.31		55.31	

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