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## Detection and quantification of levoglucosan in atmospheric aerosols: A review

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**Abstract** Levoglucosan is a tracer for biomass burning sources in atmospheric aerosol particles. Therefore, much effort has been recently put into developing methods for its quantification. This review describes and compares both established and emerging analytical methods for levoglucosan quantification in ambient aerosol samples, with the special needs of the environmental analytical chemist in mind.

**Keywords** Levoglucosan · Aerosols · Source apportionment · Bioanalytical methods

**Abbreviations** BSTFA: Bis(trimethylsilyl) trifluoroacetamide · CCN: Cloud condensation nuclei · CE: Capillary electrophoresis · DCM: Dichloromethane · ESI: Electrospray ionization · FID: Flame ionization detector · GC: Gas chromatography · HPLC: High-performance liquid chromatography · IC: Ion chromatography · IEC: Ion-exclusion chromatography · LC: Liquid chromatography · LOD: Limit of detection · LOQ: Limit of quantification · MRM: Multiple reaction monitoring · MS: Mass spectrometry · MSTFA: N-Methyl-N-trimethylsilyltrifluoroacetamide · PAD: Pulsed amperometric detection · PDA: Photodiode array · S/N: Signal-to-noise ratio · SIM: Single ion monitoring · THF: Tetrahydrofuran · TMCS: Trimethylchlorosilane · TMSI: N-Trimethylsilylimidazole

### Introduction

Atmospheric aerosols (i.e., suspended particles) in general and biomass burning aerosols in particular have recently attracted extensive interest owing to their ability to affect the climate on local to global scales [1–3]. These climatic

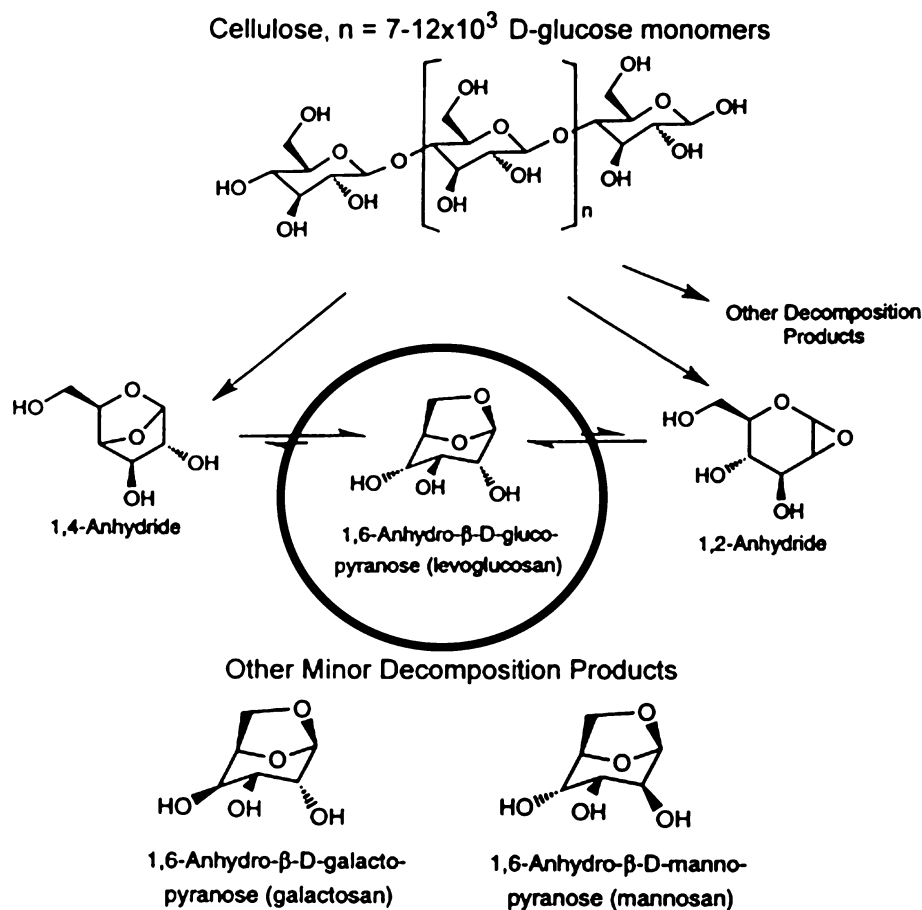
effects include a direct radiative effect due to the aerosols' ability to scatter and absorb incoming sunlight [2, 4–6], an indirect effect due to the aerosols' ability to serve as cloud condensation nuclei (CCN), increasing the cloud's reflectivity and lifetime [5, 7–9], a semidirect effect which leads to reduction in cloud cover, owing to aerosols' ability to absorb sunlight [5], changes in precipitation patterns [5, 7, 10–12], and export of pollutants and water vapor to the stratosphere [7, 12]. Trying to assess human contribution to aerosol emissions, and to assign a source to both anthropogenic and natural aerosols, is therefore important for understanding the respective contribution of different aerosol types to climate change.

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is a product of cellulose combustion, which has been recognized as a biomass burning tracer [13–18]. When cellulose is heated to over 300°C, it undergoes various pyrolytic processes, yielding a highly combustible tar, a major constituent of which is levoglucosan, a dehydrated glucose containing a ketal functional group (Fig. 1) [19]. Some of the levoglucosan is consumed in various reactions during combustion but it is nonetheless emitted in large quantities in the resulting smoke aerosol. Therefore, it can be utilized as a specific tracer for the presence of emissions from a biomass burning source in atmospheric particulate matter [15–17]. Unlike other indicators used for the same purpose, levoglucosan is source-specific to burning of any fuel containing cellulose. Combustion of other materials (e.g., fossil fuels) or biodegradation and hydrolysis of cellulose do not produce levoglucosan [13]. Levoglucosan is relatively stable in the atmosphere, showing no decay over 10 days in acidic conditions, similar to those of atmospheric liquid droplets [14]. Levoglucosan is also used in other fields of chemistry and engineering, such as pyrolysis and fire-retardants research [19–26], biofuel research [27–32], biology [33–35], organic synthesis [33, 36–40] and as a biomass burning tracer in sediment analysis for the paleorecord [13].

For these reasons, increasing effort has been put into levoglucosan quantification in recent years. In this paper we focus on levoglucosan quantification in atmospheric

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**Fig. 1** 1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan) (circled) is an abundant product of cellulose combustion temperatures above 300°C. Levoglucosan's stereoisomers, mannosan and galactosan, are shown at the bottom. (From Shafidazeh [19])



aerosol particles and review the various methods that have been developed to this end. These methods can be roughly separated into gas chromatography (GC) methods and aqueous-phase methods. GC methods, utilizing mostly a mass spectrometer as a detector, give good separation and sensitivity, and are the most commonly used methods for levoglucosan quantification, but they require long preparation, dry conditions and expensive equipment. To overcome these issues, and to facilitate atmospheric aerosol research, new methods have been developed which mostly use aqueous-phase extraction of samples, and can be applied to wet samples. In these methods the sample is either analyzed as is, or is separated by liquid chromatography (LC), and levoglucosan is detected by various detectors. This review will describe both the established GC-mass spectrometry (MS) methods and emerging aqueous-phase methods, and discuss their relative merits and shortcomings from the point of view of atmospheric aerosol research.

## GC methods

GC separation for the detection and quantification of levoglucosan is to date the most commonly used method, in conjunction with various detectors, the most popular of which is a mass spectrometer. In early pyrolysis research, trimethylsilylation followed by gas-liquid chromatography

was used to detect levoglucosan and estimate its role in cellulose degradation. It was found that levoglucosan is a major constituent of the liquid tar produced from cellulose pyrolysis at over 300 °C, and it was recognized as an important intermediate as well as product in cellulose and wood combustion [19, 41].

Simoneit et al. [15–17] were among the first to recognize the usefulness of levoglucosan as a tracer for biomass burning in atmospheric aerosol. In their studies quartz fiber filters were extracted by ultrasonic agitation into dichloromethane (DCM) or hexane, followed by a benzene/2-propanol mixture (3:1) [16], or by benzene/methanol or DCM/methanol mixtures [15]. The extract was reduced in volume using a rotary evaporator and then dried under nitrogen flow, and silylated using bis(trimethylsilyl)trifluoroacetamide (BSTFA) with pyridine. Separation and detection was performed using GC-MS, against a standard. The ion fragments  $m/z=204$  and 217 of the levoglucosan trimethylsilyl derivative were used in single ion monitoring (SIM) mode for better detection in noisy chromatograms. The uncertainty of levoglucosan concentrations and its limit of detection (LOD) were not reported.

A similar method was used also by Fraser and Lakshaman [14], Oros and Simoneit [42, 43], Fine et al. [44] and Nolte et al. [45]. Graham et al. [46, 47] used a similar method for detection of several compounds, including levoglucosan. The two main differences in their method, compared with the one already described, is the use of methanol or water

followed by DCM for extraction by vortex agitation, and the use of phenyl- $\beta$ -D-glucoside as an internal standard for recovery determination. Graham et al. reported a limit of quantification (LOQ) of 0.04 ng/m<sup>3</sup>, and an uncertainty of 20%, based on duplicate precision. In some studies 1% trimethylchlorosilane (TMCS) was used as a catalyst to silylation [42, 43, 46, 47].

Simpson et al. [48] have recently discussed what they consider to be a possible lack of thorough validation procedures for levoglucosan analysis by the GC-MS methods, and suggested one such validation. Urban aerosol particles sampled on Teflon filter membranes were spiked with sedoheptulosan, serving as a recovery standard. The filters were dried and extracted into ethyl acetate containing 3.6 mM trimethylamine by ultrasonic agitation. The extract was reduced in volume, spiked with the internal standard 1,5-anhydro-D-mannitol and silylated using *N*-trimethylsilylimidazole (TMSI). The GC-MS analytical procedure was similar to the one used by Simoneit et al. [16]. The recovery reported for levoglucosan was 69±6% for filters spiked with a standard, the detection limit at a signal-to-noise ratio (S/N) of 3 was 0.1 µg/ml or 3.5 ng/m<sup>3</sup> (for 10-l/min sampling rate and 24 h sampling). The reproducibility for samples was 4.9%. They reported that the use of *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) or BSTFA with 1% TMCS and pyridine was impaired by the presence of the solvent (ethyl acetate) and took substantially longer (6 h) for complete derivatization of levoglucosan compared with TMSI (0.5 h). However, while TMSI silylation required a 50:1 split ratio, silylation by MSTFA allowed splitless injection and an improved 25 ng/ml detection limit, but was less robust for the ethyl acetate extracts. It was also found that levoglucosan recovery (by spiking filters with standard) from Teflon filters was better than from quartz fiber filters.

In a thoroughly validated procedure, Zdráhal et al. [49] employed GC-MS for identification and GC flame ionization detection for quantification of levoglucosan and its isomers—mannosan and galactosan. Extraction by ultrasonic agitation of the quartz fiber filter samples into DCM was preferred since DCM evaporates easily and avoids extraction of compounds which might later stick to the GC injector and column. 1,2,3-Trihydroxyhexane was used as a recovery standard and added prior to extraction. Dried extracts were dissolved in pyridine and silylated. BSTFA was found to produce incomplete derivatization of levoglucosan. TMSI and MSTFA (1% TMCS) with pyridine showed full derivatization after 1 h, shorter than the procedure reported by Simpson et al. [48] possibly owing to the different solvent used. 1-Phenyldodecane was added after derivatization as an internal standard. Recovery of levoglucosan, determined by spiking a filter with standard, was found to be 60%, the reproducibility for standard solutions was 2% and for segments of the same sample filter 5%.

GC-MS/MS analysis was utilized by Pashynska et al. [50], who extracted quartz fiber filter samples into a DCM/methanol mixture (80:20, v/v) after spiking with methyl- $\beta$ -L-arabinopyranoside recovery standard. Extracts were dried, dissolved in a DCM/methanol mixture (50:50, v/v)

and dried again, to be silylated using MSTFA + 1% TMCS and pyridine. Levoglucosan recovery of 90±2.4% was determined by spiking filters with a standard. GC was used for separation, and ion-trap MS/MS for detection, at *m/z*=217 in both SIM and multiple reaction monitoring (MRM) modes. The MRM mode gave S/N>10 for the smallest concentrations found in urban summer aerosol samples, and the SIM mode gave twice that, but without the elaborate spectral information allowed by the MRM mode. No detection limit was reported, but the lowest levoglucosan concentration reported was 9.1 ng/m<sup>3</sup>. The reproducibility for segments of the same filter sample was 5% for the lower loadings.

All the previously reported methods separate levoglucosan from its isomers mannosan and galactosan.

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## Aqueous-phase methods

### Electrospray ionization–MS methods

Electrospray ionization (ESI) is a relatively new technique for introducing liquid-phase samples into the mass spectrometer, and it allows soft ionization of highly polar and nonvolatile compounds [51]. Gao et al. [52] were the first to report the use of ESI-MS for levoglucosan quantification in water extracts of biomass burning aerosols. They extracted Teflon filter samples into deionized water by mechanical shaking, before introducing the extract into an ESI ion trap mass spectrometer. They identified seven polyhydroxy compounds, including levoglucosan, mannitol and glucose, each giving a single pseudomolecular (sodium adduct) peak, which was later used for quantification against an authentic standard. However, since the molecules did not undergo fragmentation, it was not possible to positively identify them solely by the pseudomolecular peak in the mass spectrum. To assist identification, the same extracts were analyzed also by ion chromatography (IC) with pulsed amperometric detection (PAD), and the ratio of the IC-PAD response to the MS response for a standard was used to identify the different compounds in the samples. A LOD of 0.2 µg/m<sup>3</sup> (or 0.06 µg/ml, according to the collection and extraction procedure) for levoglucosan and a worst case precision of 12% were achieved. Palma et al. [53] employed ESI-MS/MS for the determination of levoglucosan in fog water using MS/MS for better identification. Separation of levoglucosan from its isomers, mannosan and galactosan, was not achieved, and the complexity of the fog water matrix resulted in MS/MS spectra that differed between sample and standard.

A straightforward combination of high-performance LC (HPLC) separation and ESI-MS detection was reported by Dye and Yttri [54], who used HPLC-ESI high-resolution MS for separation and detection of levoglucosan, mannosan and galactosan. They used a reversed-phase C<sub>18</sub> column with water and acetonitrile gradient elution for separation. Fragmentation of the compounds was achieved, yielding a distinct mass spectrum for each isomer. Since levoglucosan

and mannosan were partly coeluted, masses 113 and 129  $m/z$  (respectively) were used to achieve baseline separation between the two. A lower cone voltage was used to eliminate fragmentation and gain better sensitivity. In order to have both sensitivity and separation, the cone voltage was cycled during the run. The LOQ reported for levoglucosan was 26 ng/m<sup>3</sup> ( $m/z=113$ ) or 5 ng/m<sup>3</sup> ( $m/z=161$ ) S/N=10. Samples were collected on non-pre-baked quartz fiber or Zefluor Teflon filters, and extracted by ultrasonic agitation into tetrahydrofuran (THF).

#### Microchip capillary electrophoresis with PAD

García et al. [55] reported the use of microchip capillary electrophoresis (CE) with pulsed amperometric detection (PAD) for detection of levoglucosan in water extracts of smoke samples created by burning wood in the laboratory and collected on quartz fiber filters. The LOD reported was 2.7 µg/ml (S/N=3), and levoglucosan was separated from glucose and galactosan/mannosan; however, mannosan was not separated from galactosan. Levoglucosan was not detectable by this method in rural ambient samples, owing to differences in conductivity between the sample extract and the running electrolyte.

#### Ion-exclusion chromatography–HPLC–*photodiode array*

Schkolnik et al. [56] recently developed a method based on HPLC analysis of water-extracted filter samples and rainwater samples. Ion-exclusion chromatography (IEC)–HPLC was used for separation. In IEC, the column's resin contains acidic functionalities, which form negatively charged hydration spheres when wetted. While strong, highly ionized acids are repulsed by the hydration spheres and thus pass quickly through the column, nonionic compounds, such as polyhydroxy compounds, can enter the resin network and are retained, being eluted in decreasing order of acidity (decreasing number of OH groups). A photodiode array (PDA) at 194 nm was used for detection of polyhydroxy compounds. Levoglucosan, erythritol, arabitol, mannitol, glucose and 2-methylerythritol were easily separated, with mannosan appearing as a shoulder on the levoglucosan peak, which could be resolved using a multi-Gaussian peak fit. Coelution of levoglucosan with 2-methylthreitol was overcome by knowing the 2-methylerythritol to 2-methylthreitol ratio. Particles sampled on quartz fiber or Nuclepore polycarbonate filters were extracted into water by vortex agitation. The resulting extracts as well as rainwater samples were passed through a solid-phase extraction cartridge to remove polyacids that interfered with detection. Levoglucosan and 2-methylerythritol were quantified in samples with a 15% uncertainty and concentrations were compared and found to agree with values obtained by GC-MS analysis of parallel samples (M. Clayes, unpublished data). The limit of detection was 0.5 µg/ml, which allowed detection of levoglucosan in

ambient samples under smoky or semismoky conditions, but not under clean conditions.

#### IC-HPLC-PAD

Bauer et al. (unpublished results) conducted levoglucosan analysis by IC-PAD, using a column especially designed for sugar analysis (Dionex CarboPac PA10 anion-exchange column), with 30–40 mM NaOH gradient elution. This procedure requires the use of a guard column and washing the system with 250 mM NaOH after each run. A validation for this method was not reported.

#### H NMR

Levoglucosan was detected and quantified by H NMR in extracts of smoke samples by Graham et al. [47], using a method published by Decesari et al. [57]. Aerosol sampled on quartz fiber filters during forest fires was extracted into D<sub>2</sub>O, containing 0.05% (w/w) sodium 3-(trimethylsilyl)–2,2,3,3-*d*<sub>4</sub>-propionate as internal standard. The spectra were obtained using a 300-MHz spectrometer in a 5-mm probe. In the smoke sample's spectrum, a sharp peak appears at 5.4 ppm, corresponding to a peak found in the levoglucosan standard. The concentration of levoglucosan was estimated by comparing the integral of this peak with that of the internal standard. A validation was not performed for the method, and the possibility that the 5.4-ppm peak also belongs to compounds other than levoglucosan still has to be examined. However, levoglucosan concentrations from H NMR analysis agreed reasonably with values obtained from GC-MS analysis, with H NMR values slightly underestimated (0.87 of the GC-MS values).

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### Comparison of various attributes of the analytical methods described

For a summary of the following discussion see Table 1.

#### Extraction and recovery

Biomass burning aerosols contain a large fraction of water-soluble organic carbon arising from numerous compounds, the majority of which have not as yet been identified [18, 47]. These water-soluble compounds may play an important role in the aerosol's activity as CCN. For this reason it is beneficial to be able to quantify the water-available fraction of the aerosol. Being able to work with wet samples, such as rain, fog or cloud water, is also highly desirable, in order to understand the involvement of biomass burning aerosols in cloud formation and precipitation. It is therefore preferable to use a quantification method which allows water extraction of the samples and analysis of wet samples. Such methods are IEC-HPLC-PDA [56], ESI-MS [52, 53], H NMR [47, 57], CE-PAD

**Table 1** Comparison of various attributes of the analytical methods

Reference	Method <sup>a</sup>	Water extraction and wet samples	Recovery (%) <sup>b</sup>	Separation of levoglucosan, mannosan and galactosan	LOD (LOQ) ( $\mu\text{g/ml}$ )	Additional detectible polyhydroxy species	Short and simple sample preparation and analysis
Schkolnik et al. [56]	IEC-HPLC-PDA	Yes	95 $\pm$ 3	Levoglucosan and mannosan resolved	0.5 (1.0)	Mannitol, arabitol, erythritol, 2-methylethritol	Yes
Bauer et al. (unpublished results)	IC-HPLC-PAD	Yes	Not reported	Separated	Not reported	Not reported	Yes
Decesari et al. [57], Graham et al. [47]	H NMR	Yes	Not reported	Not reported	Not reported	Not reported	Yes
Gao et al. [52]	ESI-MS + HPLC-PAD	Yes	Not reported	Not reported	0.06	1,4:3,6-Dianhydro- $\alpha$ -d-glucopyranose, levoglucosenone, glucose, mannitol, xylitol, glycerol	Yes
Simoneit and Elias [15]	GC-MS	No	Not reported	Full separation	Not reported	Not reported	Not reported
Graham et al. [46]	GC-MS	Yes <sup>c</sup>	Not reported	Full separation	(0.34)	Numerous anhydrosugars, sugars and sugar alcohols	Not reported
Pashynska et al. [50]	GC-MS-MS	No	90.0 $\pm$ 2.4–97.0 $\pm$ 4.0	Full separation	Not reported	Numerous anhydrosugars, sugars and sugar alcohols	Yes
Zdrahal et al. [49]	GC-FID	No	60	Full separation	Not reported	sugar alcohols	Yes
Simpson et al. [48]	GC-MS	No	69 $\pm$ 6	Not reported	0.1	Not reported	Yes
Dye and Yitry [54]	HPLC-ESI-HRMS	No	99	Full separation	0.03	Not reported	Yes
Palma et al. [53]	ESI-MS-MS	Yes	Not reported	No separation	NA <sup>d</sup>	Not reported	Yes
Garcia et al. [55]	CE-PAD	Yes	Not reported	Levoglucosan separated. Mannosan and galactosan comigrate	2.7 <sup>d</sup>	Glucose	Yes

<sup>a</sup>For an explanation of the acronyms, see the list of Abbreviations<sup>b</sup>Based on analysis of filters spiked with standard<sup>c</sup>Applied by Graham et al. [47]<sup>d</sup>No quantitation in ambient samples reported

[55], IC-PAD (Bauer et al., unpublished results) and in at least one instance this was accomplished even with GC-MS [47].

The recovery yield of each extraction solvent must also be considered. Since levoglucosan is a polyhydroxy polar compound, polar hydroxyl-containing solvents are expected to be effective for its extraction. The recovery is most commonly tested by spiking blank filters with a standard and subjecting it to the analytical procedure to be used. For levoglucosan, extraction by water yields a recovery of  $95\pm 3\%$  [56]. A DCM/methanol mixture (80:20, v/v) has also proved to be an effective extraction solvent, yielding  $90.0\pm 2.4$ – $97.0\pm 4.0\%$ , depending on the amount of levoglucosan applied to the filter [50]. Ethyl acetate yielded a lower recovery of  $69\pm 6\%$  [48], and DCM was shown to have an even lower recovery of 60% [49]. Dye and Yittri [54] achieved 99% recovery using THF. Comparing extraction efficiencies of levoglucosan from real samples, they found that DCM or a 50% THF-in-water solution gave recoveries smaller by 40–60%. These workers observed lower recoveries when sampling on quartz fiber filters, compared with Teflon filters, in accordance with results reported by Simpson et al. [48].

### Separation

Levoglucosan has two stereoisomers, mannosan and galactosan, that pose a separation challenge in levoglucosan quantification. These stereoisomers are present in biomass burning aerosols in much smaller quantities than levoglucosan [42, 47, 50], and they are expected to have chemical and physical properties similar to those of levoglucosan. Therefore, some argue that it is not necessary to separate them, while others are more interested in their separation. Typically, GC methods give full separation of the three stereoisomers [15, 46, 49, 50]. This was also achieved by the HPLC-ESI-MS method [54]. ESI-MS methods which do not use HPLC separation are unable to separate between compounds which have the same pseudomolecular  $m/z$  and share some fragmentation masses [52, 53]. With use of IEC-HPLC mannosan, but not galactosan, was resolved from levoglucosan, using multi-Gaussian peak fit analysis of the chromatogram [56]. Levoglucosan was separated from its stereoisomers using CE [55], but mannosan and galactosan themselves comigrated and could not be separated. Separation of levoglucosan, mannosan and galactosan by IC-PAD was reported (Bauer et al., unpublished results).

### Sensitivity

Sensitivity is an important factor when it comes to environmental samples. The best sensitivities (in terms of limit of detection) reported for levoglucosan detection were 0.03 and 0.06  $\mu\text{g}/\text{ml}$ , achieved by ESI-MS [52, 54], and

allowing quantification of levoglucosan in both smoky and background samples. A more moderate sensitivity of 0.5- $\mu\text{g}/\text{ml}$  LOD was achieved by IEC-HPLC-PDA [56]. Such sensitivity allowed quantification of levoglucosan in smoky to semismoky conditions, but not under clean conditions. Reported sensitivities of GC-MS methods are on the scale of 0.1- $\mu\text{g}/\text{ml}$  LOD [48] or 0.34- $\mu\text{g}/\text{ml}$  LOQ [46]. Owing to very small injection volumes, these allow quantification of levoglucosan even in background levels [49, 50]. CE-PAD yielded 2.7- $\mu\text{g}/\text{ml}$  LOD, which sufficed for detection of levoglucosan in laboratory-generated smoke, but not in ambient samples.

### Uncertainty

Many factors contribute to the uncertainty in the analysis of ambient aerosol samples, and to variability of results. Apart from ambient conditions and sampling-associated uncertainties, the analytical method itself may suffer from sample inhomogeneity, matrix complexity, codetection of unknown compounds and losses during sample preparation. To deal with the latter, some researchers use an internal standard, such as phenyl- $\beta$ -D-glucoside [47], 1,5-anhydro-D-mannitol [48] and  $\beta$ -L-arabinopyranoside [50]. Matrix complexity can be reduced either by separation prior to detection, or by removing interfering compounds from the extract prior to analysis, e.g., by solid-phase extraction [56]. Sample inhomogeneity is usually accounted for by either running a precision test for different portions of one sample, or by constantly analyzing replicates of each sample.

In calculating the uncertainty of reported results, one has to take into account several contributions, such as injection uncertainty of both standard and sample, variability within the sample, linearity uncertainty when using a calibration curve, and the recovery uncertainty. Unfortunately, most studies report only sample replicate precision. Reproducibility values found for GC-MS are 20% [46, 47], 2–5% [50] and 5% [48]. The last two, however, report 2.4–4.0 and 9% reproducibilities (correspondingly) for the recovery, which should also be taken into account. Precisions for ESI-MS are 2–12% reported by Gao et al. [52] and 4–6% for standard injections with 2–12% for sample triplicates reported by Simpson et al. [48]. Schkolnik et al. [56] reported a 15% uncertainty, taking into account standard and sample injection precision, sample reproducibility, recovery uncertainty and coelution correction uncertainty.

### Analysis of additional polyhydroxy species and use of multitechnique analysis

Owing to the highly complex nature of biomass burning aerosol's organic matrix, an effort has been made to characterize as many compounds as possible, still leaving a large fraction unidentified [18]. When selecting an ana-

lytical method, some give great weight to the number of compounds quantifiable by that method and by other methods, for the same or parallel samples. Others are interested in smaller sets of compounds, containing a certain class (e.g., water-soluble compounds), and allowing quicker and simpler analysis. Another approach altogether is to quantify functional groups rather than individual compounds [58, 59].

It is evident that the largest number of different polyhydroxy compounds can be quantified using GC-MS methods. These methods allow the determination of a wide range of anhydrosugars, sugars and sugar alcohols [47, 50]. Quantification of numerous acids is also achieved by derivatizing the extracts with  $\text{CH}_3\text{ONH}_2$  prior to silylation [47]. It is also possible to analyze samples for homologous series of various hydrocarbons, including polycyclic aromatic hydrocarbons, carboxylic acids, diterpenoid and triterpenoid ketones and various hydroxylated and polar organic compounds [18]. Elemental analysis (such as proton induced X-ray emission or inductively coupled plasma atomic emission spectroscopy) of the same or parallel samples can be used to determine inorganics [52, 60].

In addition to levoglucosan, Garcia et al. [55] were able to detect also glucose using CE-PAD and Gao et al. [52] also quantified 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, levoglucosenone, glucose, mannitol, xylitol and glycerol using ESI-MS. Schkolnik et al. [56] were able to detect also mannitol, arabitol, erythritol and 2-methyerythritol using IEC-HPLC-PDA. In addition, their method allows performing a regular IC analysis for the same sample extracts, thus extending the applicability of the method for quantifying major inorganic ions as well as a number of aromatic and aliphatic mono-, di- and tri acids [61]. This allowed a detailed view of the water-soluble fraction of the aerosol's major identifiable compounds. Such an extensive analysis was also allowed by the IC-PAD method (Bauer et al., unpublished results). Decesari et al. [47, 57] offer a new approach, quantifying functional groups rather than individual molecules using H NMR. Using their method they were able to both determine levoglucosan and the total amount of water-extractable functional groups, such as Ar-H, H-C-O, H-C=C- and H-C.

#### Applicability for atmospheric samples

Most of the methods reviewed here are applicable to at least some kind of atmospheric sample. This excludes the microchip-CE-PAD method, which is still only applicable to laboratory-generated smoke samples [55]. ESI-MS and GC-MS methods were applied successfully to a range of samples containing both smoky and background ambient aerosol [15, 47, 50, 52, 54]. The IEC-HPLC-PDA method has been applied successfully to smoky and semismoky samples, but as yet not to background samples. It was also successful in analyzing rainwater samples [56]. Urban samples were analyzed by IC-PAD (Bauer et al., unpublished results). Fog water sample analysis was reported using ESI-MS/MS [53].

#### Method's simplicity

An important factor in choosing an analytical method is the availability of equipment and skills required for the method. Almost as important is the complexity and length of sample preparation and analysis, which may determine the number of samples that could be analyzed or the time required to analyze a given set of samples.

While GC-MS analysis yields excellent results in terms of separation, sensitivity and number of species analyzed, all GC-MS methods reported include repetitive extractions into mostly organic solvents, drying of the sample, and derivatization (a time- and reagent-consuming process) prior to analysis, which leads to a cumbersome and time-demanding process [18, 42, 45, 46, 48, 50]. ESI-MS methods show the potential of being simpler and less time-consuming, and they may also exhibit good separation and sensitivity if used in conjugation with HPLC [54]. However, ESI-MS is still a relatively new and expensive technology, not commonly found in analytical laboratories, which makes it less accessible for use. The IEC-HPLC-PDA method, on the other hand, is a method readily available to many researchers, as the equipment needed is very common, and relatively inexpensive, and a relatively short and simple preparation is required. Unfortunately, the method's sensitivity is as yet lower than that of MS methods, and some separation problems require special consideration [56]. IC-PAD can also allow straightforward analysis using common HPLC equipment, however, it is yet to be validated (Bauer et al., unpublished results). Microchip CE-PAD shows great promise for short and simple analysis, and perhaps even online analysis applications [55]. However, this method still has to be modified to allow analysis of ambient samples. Another method which is relatively straightforward, simple and widely available is the H NMR method [47, 57]. However, a validation for this method is yet to be reported with respect to levoglucosan analysis.

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## Conclusions

Levoglucosan detection and quantification in ambient aerosol samples poses a challenge in many respects. While it is currently hard to find a method which combines good separation and sensitivity, and is also widely available, simple and time-saving, it is possible for researchers to choose from available and emerging methods the one which applies best for their needs. Workers interested in a detailed organic analysis of a small set of background to smoky samples could choose GC-MS analysis. Others, interested mostly in levoglucosan, inorganic ions and carboxylic acids in a large set of water-extracted aerosols or wet samples, collected under smoky to semismoky conditions, might choose the IEC-HPLC-PDA method. Ones who have access to HPLC-ESI-MS equipment could enjoy the combined merits of short preparation, good separation and high sensitivity, when interested in complete separation of levoglucosan from its isomers in concentrations

ranging from background to polluted. It is also to be expected that further development will be done for the newer methods described here, to ultimately produce a greater number of choices for scientists interested in levoglucosan quantification.

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