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Atmospheric Measurement Techniques Discussions

An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples

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Abstract

The monosaccharide anhydrides (MAs) levoglucosan, galactosan and mannosan are products of incomplete combustion and pyrolysis of cellulose and hemicelluloses, and are found to be major constituents of biomass burning aerosol particles. Hence, ambient aerosol particle concentrations of levoglucosan are commonly used to study the influence of residential wood burning, agricultural waste burning and wild fire emissions on ambient air quality. A European-wide intercomparison on the analysis of the three monosaccharide anhydrides was conducted based on ambient aerosol quartz fiber filter samples collected at a Norwegian urban background site during winter. Thus, the samples' content of MAs is representative for biomass burning particles originating from residential wood burning. The purpose of the intercomparison was to examine the comparability of the great diversity of analytical methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples. Thirteen laboratories participated, of which three applied High-Performance Anion-Exchange Chromatography (HPAEC), four used High-Performance Liquid Chromatography (HPLC) or Ultra-Performance Liquid Chromatography (UPLC), and six resorted to Gas Chromatography (GC). The analytical methods used were of such diversity that they should be considered as thirteen different analytical methods. All of the thirteen laboratories reported levels of levoglucosan, whereas nine reported data for mannosan and/or galactosan. Eight of the thirteen laboratories reported levels for all three isomers.

The accuracy for levoglucosan, presented as the mean percentage error (PE) for each participating laboratory, varied from −63 to 23 %; however, for 62 % of the laboratories the mean PE was within ±10 %, and for 85 % the mean PE was within ±20 %. For mannosan, the corresponding range was −60 to 69 %, but as for levoglucosan, the range was substantially smaller for a subselection of the laboratories; i.e., for 33 % of the laboratories the mean PE was within ±10 %. For galactosan, the mean PE for the participating laboratories ranged from −84 to 593 %, and as for mannosan 33 % of the laboratories reported a mean PE within ±10 %.

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The variability of the various analytical methods, as defined by their minimum and maximum PE value, was typically better for levoglucosan than for mannosan and galactosan, ranging from 3.2 to 41 % for levoglucosan, from 10 to 67 % for mannosan, and from 6 to 364 % for galactosan. For the levoglucosan to mannosan ratio, which may be used to assess the relative importance of softwood vs. hardwood burning, the variability only ranged from 3.5 to 24 %.

To our knowledge, this is the first major intercomparison on analytical methods used to quantify monosaccharide anhydrides in ambient aerosol filter samples conducted and reported in the scientific literature. The results show that for levoglucosan the accuracy is only slightly lower than that reported for analysis of SO_4^{2-} on filter samples, a constituent that has been analyzed by numerous laboratories for several decades, typically by ion chromatography, and which is considered a fairly easy constituent to measure. Hence, the results obtained for levoglucosan with respect to accuracy are encouraging and suggest that levels of levoglucosan, and to a lesser extent mannosan and galactosan, obtained by most of the analytical methods currently used to quantify monosaccharide anhydrides in ambient aerosol filter samples, are comparable.

Finally, the various analytical methods used in the current study should be tested for other aerosol matrices and concentrations as well, the most obvious being summertime aerosol samples affected by wild fires and/or agricultural fires.

1 Introduction

The monosaccharide anhydrides (MAs) levoglucosan, galactosan and mannosan are products of the incomplete combustion and pyrolysis of cellulose and hemicelluloses, and are thus constituents of biomass burning (BB) aerosol (Simoneit et al., 1999). The presence of MAs has been demonstrated in emissions from wood combustion (Oros and Simoneit, 1999; Fine et al., 2001; Nolte et al., 2001; Schmidl et al., 2008; Frey et al., 2009; Gonçalves et al., 2010, 2011; Orasche et al., 2012) as well as from wildfires, prescribed and agricultural fires (dos Santos et al., 2002; Gao et al., 2003; Sillanpää

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et al., 2005; Mazzoleni et al., 2007; Sullivan et al., 2008; Alves et al., 2010; Saarnio et al., 2010a; Vicente et al., 2012). Recently, it has been shown that combustion of peat (Iinuma et al., 2007; Kourtchev et al., 2011) as well as of certain types of brown coal (Fabbri et al., 2009) could be additional sources of ambient aerosol concentrations of MAs in regions where such fuels are utilized.

Levoglucosan exhibits the highest concentration of the MAs in the BB aerosol; consequently, it has been applied for source apportionment of ambient particulate matter (PM). Additional information can be drawn from the PM MAs pattern, e.g., it has been used to estimate the impact from combustion of different wood types; however, no clear picture of the variability of MAs concentrations and ratios from wood combustion has been found. Some studies have reported a high variability depending on burning conditions or type of wood with filtration based sampling (Schmidl et al., 2008; Orasche et al., 2012, 2013) or by application of aerosol mass spectrometry (Weimer et al., 2008; Elsasser et al., 2013). Other studies have shown relatively little variation in MAs emissions during wood combustion under varying conditions (Jordan and Seen, 2005; Frey et al., 2009) or with different types of wood (Fine et al., 2001, 2002, 2004). Size distribution measurements of MAs in particulate emission samples from wood combustion have shown that most MAs are associated with PM $< 1.2\,\mu m$ (Frey et al., 2009). These results are in agreement with wintertime observations showing that most levoglucosan is present in the PM_1 fraction of the ambient aerosol (Yttri et al., 2005; Agarwal et al., 2010; Krumal et al., 2010).

The atmospheric concentration of levoglucosan is highly variable as it depends not only on the source strength, but also on meteorological parameters. During wintertime in Europe residential wood burning is the major source of levoglucosan, and the observed concentration is typically $< 1\,\mu g\,m^{-3}$ (Oliveira et al., 2007; Yttri et al., 2009; Krumal et al., 2010; Schnelle-Kreis et al., 2010; Caseiro and Oliveira, 2012; Herich et al., 2014). In the evening and during nighttime higher concentrations ($> 1\,\mu g\,m^{-3}$) can be observed (Elsasser et al., 2012; Saffari et al., 2013). Agricultural fires are reported to cause ambient levoglucosan concentrations well above $1\,\mu g\,m^{-3}$

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(Pietrogrande et al., 2013), and concentrations > 7 µg m^{-3} have been reported for haze episodes in tropical regions (Claeys et al., 2010; He et al., 2010).

Early investigations suggested that levoglucosan is resistant to atmospheric acid-catalyzed degradation (Fraser and Lakshmanan, 2000). The low vapor pressure of levoglucosan (Oja and Suuberg, 1999; Booth et al., 2011) as well as the minor impact of temperature on the observed volatility of levoglucosan in ambient PM (Ruehl et al., 2011) further support its stability and thus its suitability as a tracer species. Recent investigations on the stability of levoglucosan in aqueous solution suggest that "*oxidation of levoglucosan in atmospheric deliquescent particles is at least as fast as that of other atmospherically relevant organic compounds and levoglucosan may not be as stable as previously thought in the atmosphere, especially under high relative humidity conditions*" (Hoffmann et al., 2010; Teraji and Arakaki, 2010). Further, oligomerization of levoglucosan by Fenton chemistry in aqueous solution has been observed (Holmes and Petrucci, 2007). The decay of levoglucosan upon ageing of wood combustion aerosol has been studied in smog chamber experiments. When exposed to typical summertime OH radical concentrations, the atmospheric lifetime of levoglucosan in BB particles was found to be 0.7–2.2 days (Hennigan et al., 2010) under biomass burning plume conditions and estimated to range up to two weeks for atmospheric background conditions (Slade and Knopf, 2013). The impact of the abovementioned effects on the levoglucosan content in the (true) ambient aerosol still remains to be documented; however, these are indications that levoglucosan may be depleted in the atmosphere, and that possible degradation thus should be taken into account when using levoglucosan as a tracer of biomass burning emissions in source apportionment studies. Nonetheless, levoglucosan is a valuable tracer to investigate the impact of residential wood burning in urban (Oliveira et al., 2007; Timonen et al., 2008; Caseiro et al., 2009; Szidat et al., 2009; Bari et al., 2010; Schnelle-Kreis et al., 2010; Saffari et al., 2013), rural background (Gelencser et al., 2007; Puxbaum et al., 2007, van Drooge and Ballesta, 2009), and remote areas (May et al., 2009; Yttri et al., 2014), especially during winter, when wood combustion is used for domestic heating.

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As levoglucosan is commonly used as a tracer of emissions from biomass combustion, increasing efforts have been put into levoglucosan quantification during the last decade. Gas chromatographic (GC) methods were established since the end of the last century, whereas liquid chromatographic methods were more recently developed and are gaining attention. A review of existing methods was published in 2006 (Schkolnik and Rudich, 2006) and derivatization methods for analysis of MAs using GC were covered by Hsu et al. (2007). Thus, only a brief overview on actual existing methods and developments will be given here.

Gas chromatography/mass spectrometry (GC/MS) methods for separation and quantification of MAs are widespread. Most GC methods used for analysis of MAs in environmental samples make use of solvent extraction followed by trimethylsilylation (Simoneit et al., 1999; Pashynska et al., 2002; Simpson et al., 2004; Medeiros and Simoneit, 2007). Reactive pyrolysis, i.e., thermally assisted alkylation of MAs, established in pyrolysis research (Fabbri et al., 2002), has also been applied to environmental samples (Blazso et al., 2003), and more recently, thermal extraction methods have been developed. Lin et al. (2007) investigated solid-phase microextraction for pre-concentration of levoglucosan from filter samples prior to GC analysis, whereas Orasche et al. (2011) developed a method for in situ derivatization of MAs in filter samples followed by GC/MS. The most recent advance was made by Ma et al. (2010), who developed a two-dimensional GC method, which uses heart-cutting and thermal extraction of MAs from filter samples without the need of chemical derivatization.

High-performance liquid chromatography combined with mass spectrometry (HPLC/MS) and high-performance anion-exchange chromatography (HPAEC) are the most commonly used methods for analysis of MAs in extracts based on polar solvents. Methods such as capillary electrophoresis with pulsed amperometric detection (CE-PAD) (Garcia et al., 2005), chloride attachment in liquid chromatography combined with negative ion electrospray mass spectrometry (Wan and Yu, 2007) and ion-exclusion high-performance liquid chromatography followed by spectroscopic detection (Schkolnik et al., 2005) have been reported in the scientific literature but do not seem

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to be widely applied to MA analysis. Gao et al. (2003) were the first to report the use of electrospray ionization-mass spectrometry (ESI-MS) for quantification of MAs, and, at present, HPLC combined with mass spectrometric (Dye and Yttri, 2005; Larsen et al., 2006; Wan and Yu, 2007; Piot et al., 2012) or aerosol charge detection (HPLC-ACD) (Dixon and Baltzell, 2006) are widespread. HPAEC coupled with pulsed amperometric detection (PAD) (Engling et al., 2006; Caseiro et al., 2007; Iinuma et al., 2009; Piazzalunga et al., 2010) or with mass spectrometric detection (HPAEC-MS) (Saarnio et al., 2010b) have been employed more recently.

The objective of the current intercomparison was to examine the comparability of the great diversity of analytical methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples.

2 Experimental

2.1 Site description and measurement period

Aerosol filter samples were collected at the urban background site Kjeller (59°58′ N, 11°3′ E), on the outskirts of the small town of Lillestrøm (20 000 inhabitants), located 20 km east of Oslo (Norway). The samples were collected during the period 11–16 December 2008. The sampling inlets were installed approximately 4 m a.g.l.

2.2 Aerosol filter samples collection, storage, preparation, and shipment

Six ambient aerosol filter samples were provided using two high-volume samplers with Total Suspended Particulate Matter (TSP) inlets collecting aerosols on quartz fibre filters (Munktel MK 360; 150 mm in diameter, batch number 403743). The instruments were operated at a flow rate of 21.5 $m^3 h^{-1}$. The sampling time ranged from 24 to 48 h.

After exposure, the filter samples were folded once, with the exposed side facing inwards, wrapped in aluminium foil, put in a zip-lock polyethylene bag and stored in a freezer at −18 °C to prevent any form of degradation of the analytes. Two field blanks

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were collected, which were treated in exactly the same manner regarding handling, transport and storage as the filters being exposed.

Each of the sampled filter samples was divided into 16 equally large sectors, providing a total of 96 sectors, each sector with an exposed area of 9.6 cm^2. A 1.0 cm^2 punch was taken from each of the 16 sectors to perform a homogeneity test of the filters subjected to the intercomparison (Sect. 2.4.1). Hence, each of the sectors sent to the participating laboratories had an exposed filter area of 8.6 cm^2 (Fig. 1).

Each sector was given a number, which combined with the filter sample identification gave the sector a unique identification. The sectors were then assigned to the participating laboratories following a randomizing approach.

For shipment, each sector was wrapped in aluminium foil and placed in a petrislide. The six petrislides to be received by each of the participating laboratories were placed in a zip-lock polyethylene bag and sent in an envelope to the participants by mail. Those receiving the samples were directed to store them in a freezer at −18 °C until analysis. The deadline for reporting the results was set to be within 70 days after shipment.

2.3 The data set – background, scope, and application

Fifteen laboratories located in twelve different European countries reported their interest in the current intercomparison exercise and received sectors from the filter samples for analysis. Two of the fifteen laboratories did not submit results. Hence, the results presented in the current study are based on the results of thirteen different laboratories. All thirteen laboratories reported levels for levoglucosan, whereas nine reported levels for mannosan and galactosan. Eight of thirteen laboratories reported levels for all three isomers, whereas one reported for levoglucosan and mannosan, and one for levoglucosan and galactosan.

A brief overview of the various analytical methods used by the participating laboratories in the current intercomparison is provided in Table 1, including information about the method's capability to separate the isomeric compounds levoglucosan, mannosan and galactosan, the method's limit of detection (LOD), the instrument being used for

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separation and detection of the analytes, the solvent(s) used for extraction and whether derivatization of the analytes was applied. Complementary information can be found in Table B1, including extraction procedure, derivatization agent, and recovery standard. A full description of the various analytical methods can be found in Appendix A: in Sect. A1 for those using HPAEC, Sect. A2 for those using HPLC and UPLC and Sect. A3 for those applying GC.

All of the major methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples, and which have been reported in the scientific literature so far, are represented in the present intercomparison. This adds additional strength to any conclusion to be drawn from the study. In addition, the descriptions of the various methods show that none of them can be considered completely identical; i.e., they differ to a large extent with respect to crucial parameters, such as, e.g., extraction procedure and derivatization agent, to fulfill such a criterion. This, however, brings an important asset to the intercomparison, as the goal is to evaluate the comparability of the great diversity of analytical methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples. On the contrary, this great diversity prevents comparison of the performance of different subclasses of analytical methods, e.g., GC- vs. LC-based methods.

2.4 Quality assurance

2.4.1 Homogenity of filter samples

A uniformity test was performed to ensure that the two co-located filter samplers generated samples with a homogenous distribution of the analytes.

Each of the six filter samples analyzed in the intercomparison was divided into 16 equally large sectors. From each sector one 1.0 cm^2 punch was taken and subjected to levoglucosan, mannosan and galactosan analysis using the analytical method applied by lab. 1 (see Appendix A information for a detailed description of the analytical methods used by the participating laboratories). I.e., a total of 96 analyses were performed

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for each of the three isomers. The results from this uniformity test are shown in Table B2 and are briefly summarized as follows.

For levoglucosan, the mean relative standard deviation (RSD) for all six filter samples was 11 ± 2.7 %. The highest RSD was observed for filter sample 3 (16 %) and the lowest for filter sample 2 (9.1 %). For mannosan, the mean RSD was 19 ± 9.9 %, with the lowest RSD for filter sample 1 (10 %) and the highest for filter sample 4 (35 %). For galactosan, the mean RSD was 24 ± 15 %, with the lowest RSD for filter sample 2 (11 %) and the highest for filter sample 3 (45 %). Note that the percentage provided for the RSD also includes the uncertainty of the analytical method (which is < 5 %); hence, the filter homogeneity is in fact up to 5 % lower than that stated above. Two outliers were detected for galactosan (one in filter sample 4 and one in filter sample 5, respectively) and one for mannosan (filter sample 5), when running the Grubbs test for outliers. These outliers did not affect the results of the intercomparison, as the sectors from which they were taken were sent out to laboratories which either did not submit results at all or which did not submit results for mannosan (lab. 13), or the sector was not assigned to any of the participating laboratories. Consequently, the results from the homogeneity test demonstrate that the collected filter samples are sufficiently homogenous to be used for an intercomparison.

Finally, it can be questioned to which extent a 1.0 cm^2 punch from each sector is representative for addressing the homogeneity of the filter samples as it accounts for no more than 10 % of the total exposed filter area. However, the size of the punch used for the homogeneity test should not compromise the participation of various laboratories using analytical methods with detection limits varying over a wide range.

2.4.2 Outliers – Grubbs test

The Grubbs test was used to detect outliers amongst the results submitted by the various laboratories. For levoglucosan, one outlier was detected for filter samples 1 and 2 and both were reported by the same laboratory (lab. 7). For galactosan, one outlier was detected for each of the six filter samples and all were reported by the

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same laboratory (lab. 9). No outliers were observed for mannosan. Values defined as outliers were excluded from calculation of the "theoretical" median value, but included in the "measured" arithmetic mean value (see Sect. 2.5 for explanation of "theoretical" and "measured" value).

2.4.3 Samples with levels below limit of detection

Two laboratories (lab. 3 and 8) reported values of galactosan below the established detection limit of their analytical method for filter samples 3–6. These values were not included in the calculated "theoretical" median value nor in the "measured" mean value.

2.5 Calculation of the analytical methods performance

The outcomes of the intercomparison are presented in Figs. 2–4 as aggregated results, whereas the aggregated data reported by the laboratories, which are used as input for Figs. 2–4, are listed in Table B3. The results are presented in terms of the percentage error (PE); i.e., the PE was calculated for each of the participating laboratories for each of the six filter samples according to Eq. (1). The arithmetic mean PE for each laboratory, accounting for all six filters, was then subsequently calculated (Figs. 2–4).

$$\text{Percentage error (PE)} = \frac{\text{measured} - \text{theoretical}}{\text{theoretical}} \times 100 \quad (1)$$

where "measured" is the value of the analyte, e.g., levoglucosan, reported by the actual laboratory for one of the six filter samples and which is having its accuracy tested vs. the "theoretical" value. The latter value is the median value of the analyte based on the values reported by all participating laboratories (except outliers as described above). For laboratories reporting values for two or more aliquots pr. sector, the "measured" value is represented by the arithmetic mean, as this variable better reflects the variability of the method's performance. For the "theoretical" value we chose to use the median in order to limit the influence of deviating results not considered as outliers.

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The isomer splits, showing the relative contribution of each of the three monosaccharide anhydrides to the sum of the three monosaccharide anhydrides (ΣMA), and the levoglucosan to mannosan ratio are shown in Figs. 5–8 as aggregated results, whereas the aggregated data, based on those reported by the laboratories, are listed in Table B4. The results are discussed in detail in Sect. 3.

2.6 Analytical standard compounds

A different quality of standard compounds is a factor potentially affecting the comparability of an intercomparison. Results obtained using standard compounds without a given purity is of particular concern, but also batch-to-batch inconsistency is of potential importance.

In the present study, quantification standards of levoglucosan from three different manufacturers were employed, ranging from > 98 to 99 % purity. For mannosan the range of purity was 98 % to "purity not given" for standards purchased from three different manufacturers. One of the laboratories (lab. 11) used the levoglucosan standard also for mannosan and galactosan. The purity of the galactosan standards was "not provided" for all, except for that used by lab. 9 (98 % purity) and lab. 13 (99 % purity).

Nine (lab. 1, 2, 4, 5, 6, 9, 11, 12, 13) out of the thirteen laboratories used an internal standard, but only eight (lab. 1, 2, 4, 5, 6, 9, 11, 12) of them used it to account for potential loss of analytic compounds during clean up. $^{13}C_6$-labeled levoglucosan with a 98–99 % purity, purchased from two different manufacturers, was used by four laboratories (lab. 1, 2, 6, 12), whereas $^{2}H_7$-labeled levoglucosan (99 % purity) (lab. 9), $^{13}C_6$-labeled galactosan (purity not known) (lab. 1), $^{2}H_4$-labeled succinic acid (98 % purity) (lab. 5), *O*-L-xylanopyranoside (99 % purity) (lab. 4) and sedoheptulose (> 99 % purity) (lab. 11) were each used by one laboratory. Laboratory 13 used the internal standard (1-phenyldodecane, 99 % purity) to account for uncertainties in the injection volume.

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3 Results and discussion

3.1 Levoglucosan

The median theoretical concentration of levoglucosan, calculated based on the values reported by the laboratories performing analysis of the actual compound, ranged from 552 ng cm^{-2} (filter sample 6) to 1765 ng cm^{-2} (filter sample 1) (Table B3). This range corresponds to an ambient concentration of levoglucosan ranging from 120–384 ng m^{-3}, if obtained by a typical low volume sampler operating at flow rate of 38 L min^{-1} for 24 h, assuming an exposed filter area of 12 cm^2. This is within the range (60–900 ng m^{-3}) observed for European urban areas during wintertime sampling, as reported by Szidat et al. (2009).

For the laboratories extracting, analyzing and reporting values for two or more aliquots pr. sector, the repeatability was on average 4.5 ± 2.9 %. The repeatability exceeded 10 % for three of the 54 sectors, each of the three being analyzed by different laboratories (lab. 1, 3, and 13).

From Fig. 2 it can be seen that the mean PE for the various analytical methods ranged from −63 to 20 %, i.e., reflecting the accuracy of the various methods. The lowest mean PE was seen for lab. 7, for which two outliers were detected. When excluding these results from the calculation, the mean PE for lab. 7 improved from −63 to −54 %, and thus also the total range including all the methods. The mean PE was within ±10 % for eight (lab. 2, 3, 4, 6, 10, 11, 12, and 13) of the thirteen laboratories, i.e., for 62 % of the laboratories, which should be considered a narrow range, and within ±20 % for eleven (lab. 1, 2, 3, 4, 5, 6, 9, 10, 11, 12, 13) of the thirteen laboratories, corresponding to 85 %. Indeed, the accuracy reported for levoglucosan analysis is only slightly lower than the results reported for analysis of SO_4^{2-} on filter samples during the latest intercomparison (intercomparison number 30) organized by EMEP (http://www.nilu.no/projects/ccc/intercomparison/DQO-luft-30.pdf); i.e., an accuracy ranging from −23 to 40 % for the entire dataset of 64 laboratories, and from −6 to 5 % for the subselection accounting for 62 % of the laboratories. SO_4^{2-} in aerosol filter

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samples has been analyzed by numerous laboratories for several decades, typically by ion chromatography, and should be considered as a fairly easy constituent to analyze. Hence, the comparable results obtained for levoglucosan with respect to accuracy are encouraging.

In Figs. 2–4 the error bars represent the minimum and the maximum PE observed for the six samples analyzed with the respective analytical method. Hence, the range is a measure of the variability of the analytical method; i.e., the smaller the range, the better. For levoglucosan (Fig. 2) the variability ranged from 3.2 to 41 %. Two of the laboratories had a mean PE exceeding −40 %. For lab. 7 the low accuracy was accompanied by a large variability (30 %), whereas this was not the case for lab. 8 (6.5 %). For lab. 7 the combination of a low accuracy and a large variability could suggest an instrument malfunction rather than a flaw in the analytical method used. However, two of the samples reported by this laboratory were outliers, and when excluded from the calculation, the variability improved substantially (i.e., a variability of 5 %), thus a systematic underestimation could not be excluded. It should be noted that lab. 7 later found that their instrument suffered from a technical problem that caused a random loss of signals during the sample analysis. Subsequent tests revealed that previous injections of high salt-containing samples (i.e., seawater) had contaminated the instrument. The problem was resolved by a rigorous cleaning of instrument components, including working electrode, tubing, and fittings. Nevertheless, only two of the samples reported by this laboratory were considered outliers when tested; hence, the results reported from this laboratory should be included in the current dataset. There were also other laboratories experiencing difficulties of various categories during the intercomparison; e.g., lab. 1 experienced possible ion suppression, mainly of levoglucosan, which was not previously observed using the actual method, causing negatively biased concentrations as well as deviating isomer splits. Furthermore, other analytic methods used in the current intercomparison could be affected by flaws as well, except that they have passed unseen. Thus, selectively removing data from the intercomparison when being aware

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of certain problems for one laboratory but not for others cannot easily be done without introducing additional flaws to the dataset.

Despite that the great diversity of the analytical methods prevents us from comparing the performance of different subclasses of analytical methods, it cannot be neglected that a certain pattern emerges from Fig. 2. Five out of the six GC-based methods participating in the intercomparison had a mean PE above the theoretical value, ranging from 2.8–20 %. Furthermore, four of these five GC methods were based on the approach initially developed in the USA, which subsequently has been adopted by European research laboratories, involving separation by GC, detection by mass spectrometry, extraction by methanol or dichloromethane, or a combination of the two, as well as derivatization to improve the (gas) chromatographic behavior of the analyte. Despite a certain variation between laboratories, the general approach outlined above is by far the most commonly used one for analyzing levoglucosan within the research community and it also has the longest record of use. Hence, refinement and experience in using this method is expected to be more extensive than for the more recently developed LC and IC methods, for which the mean PE was below the theoretical value for five of seven methods (−63 to −1.9 %) (Fig. 2). Consequently, we should not exclude the possibility that the experience associated with a more widespread analytical method could have a profound influence on the observed pattern, and that this might be an equally important factor as any differences attributed to the choice of the analytical method itself. Given that the more recently developed LC and IC methods have been taken into service on a wider scale than at the time of the current intercomparison, a follow-up intercomparison should address any potential change in the pattern seen in Fig. 2 of the current study.

3.2 Mannosan

The median theoretical concentration of mannosan, calculated based on the values reported by the laboratories performing analysis of the actual compound, ranged from 80 ng cm^{-2} (filter sample 4) to 300 ng cm^{-2} (filter sample 1). This range corresponds

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to an ambient concentration of mannosan ranging from 17–65 ng m^{-3}, if obtained by a typical low volume sampler operating at flow rate of 2.3 m^3 h^{-1} for 24 h, assuming an exposed filter area of 12 cm^2.

For the laboratories extracting, analyzing and reporting values of mannosan for two or more aliquots pr. sample, the repeatability was on average 5.2 ± 3.9 %. The repeatability exceeded 10 % for three of the 36 samples, and was reported by two different laboratories (lab. 8, 9).

The mean PE, representing the accuracy, ranged from −60 to 69 % for the various analytical methods reporting values for mannosan (Fig. 3). This range is noticeably wider than that seen for levoglucosan (−63 to 20 %), and whereas 62 % of the laboratories reported a mean PE within ±10 % for levoglucosan, the corresponding percentage for mannosan was only 33 (i.e. for lab. 6, 10, and 11). 55 % of the laboratories reported a mean PE within ±23 % for mannosan (lab. 2, 4, 6, 10, and 11).

As described in Sect. 3.1, the "error bars" in Figs. 2–4 represent the minimum and the maximum PE observed for the actual analytical method, and thus the range is a measure of the variability of the analytical method. For mannosan the variability ranged from 9.3 to 38 %, which is a slightly smaller range than that seen for levoglucosan. For five of the nine laboratories (lab. 2, 3, 4, 8, and 11) reporting values for both levoglucosan and mannosan the variability was substantially higher, i.e., a factor of 2–6 for mannosan compared to levoglucosan. For two of the laboratories the difference was only minor (lab. 9) or non-existing (lab. 7), whereas laboratories 6 and 10 had a slightly lower variability for mannosan compared to levoglucosan.

The three GC-based methods used to determine levels of mannosan had a mean PE above the theoretical value, ranging from 2.4–69 %, thus reflecting the general pattern seen for levoglucosan, whereas it ranged from below to above the theoretical values for the LC- and IC-based methods.

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3.3 Galactosan

The median theoretical concentration of galactosan, calculated based on the values reported by the laboratories performing analysis of the actual compound, ranged from 31 ng cm^{-2} (filter sample 6) to 90 ng cm^{-2} (filter sample 1). This range corresponds to an ambient concentration of galactosan ranging from 7–20 ng m^{-3}, if obtained by a typical low volume sampler operating at flow rate of 2.3 m^3 h^{-1} for 24 h, assuming an exposed filter area of 12 cm^2.

For the laboratories extracting, analyzing and reporting values for two or more aliquots pr. sample, the repeatability was on average 8.5 ± 11 %. The repeatability exceeded 10 % for eleven of the 34 samples, and was reported by five different laboratories (lab. 2, 3, 8, 9, and 11).

The mean PE, representing the accuracy, ranged from −84 to 593 % for the various analytical methods reporting values for galactosan. This range is noticeably wider than that seen for both levoglucosan (−63 to 20 %) and mannosan (−60 to 69 %). The very high mean PE (593 %) seen for lab. 9 is consistent with the finding that all values of galactosan reported by this laboratory were found to be outliers. When excluding these data from the calculation, the mean PE range is substantially narrowed (−84–68 %), but it is still wider than for the two other isomers. Excluding the two outliers reported by lab. 7 did not have an influence on the mean PE range including all laboratories, and it only marginally improved the mean PE for lab. 7, going from −74 to −70 %. 33 % of the laboratories (lab. 4, 10, and 11) reported a mean PE for galactosan within ±10 %. This equals the percentage found for mannosan, but it is substantially lower than that observed for levoglucosan (62 %). 55 % of the laboratories (lab. 2, 3, 4, 10, and 11) reported a mean PE within ±22 % for galactosan. It should be noted that for lab. 3 and 8 the mean PE is based on the results from only two of the six filter samples, as the value was found to be below the detection limit for the other four.

As previously described (Sects. 3.1 and 3.2), the error bars in Figs. 2–4 represent the minimum and the maximum PE observed for the actual analytical method, and thus are

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a measure of the variability. For galactosan the variability ranged from 6 to 364 % when including all laboratories. For the subselection of laboratories not influenced by outliers or levels below the detection limit, the variability ranged from 16 to 112 %. For the latter subcategory of laboratories the variability for galactosan was better than that seen for mannosan for two of the laboratories (lab. 10 and 11) and poorer for the two others (lab. 2 and 4). For lab. 10, the variability was noticeably better for galactosan (16 %) also when compared to levoglucosan (41 % and 31 % for levoglucosan and mannosan, respectively).

3.4 Relative contribution of levoglucosan, mannosan and galactosan to the sum of the three isomeric compounds (ΣMA)

3.4.1 Levoglucosan to ΣMA ratio

The median theoretical relative contribution of levoglucosan to ΣMA ranged from 81–83 % for the eight laboratories from which this ratio could be derived (Table B4); i.e., laboratories not affected by outliers of any of the three isomers or by levels below the detection limit (Table B3). The levoglucosan to ΣMA ratio did not vary substantially between the laboratories included in the abovementioned subcategory. The largest difference was observed for filter sample 1 for which lab. 3 and lab. 10 reported a value of 81 % and lab. 8 a value of 87 %. This rather small difference is to be expected given that levoglucosan is by far the major MA of the three isomeric compounds reported in the literature. Lab. 7 reported values of levoglucosan for filter sample 1 and 2, which were found to be outliers; however, the levoglucosan to ΣMA ratio for these two filter samples (80 %) did not differ substantially from that of filter samples 3–6 (82–84 %), nor from the subcategory not affected by outliers. For lab. 9 the levoglucosan to ΣMA ratio ranged from 57–69 %, which is substantially lower than for the other laboratories. Indeed, lab. 9 reported levels of galactosan for filter samples 1–6, which all were found to be outliers, and a markedly high mean PE for galactosan of 593 % (Fig. 4). Lab. 9 also reported the highest mean concentration of mannosan, with a mean PE of 69 %

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(Fig. 3). Despite the fact that lab. 9 also reported the highest mean concentration of levoglucosan, the mean PE (20 %) was lower for this isomer than for the two others; hence, the lower levoglucosan to ΣMA ratios seen for lab. 9 can likely be attributed to an overestimation of mannosan and galactosan.

The mean PE, representing the accuracy, ranged from −22 to 3.2 % for the various laboratories for which the levoglucosan to ΣMA could be derived (Fig. 5). When excluding lab. 9, which reported outliers for filter samples 1–6 with respect to galactosan, this range is substantially reduced (−2.4 to 3.2 %). Excluding the two outliers detected for lab. 7 only had a minor effect on the mean PE for the actual laboratory, going from −0.4 to −0.6 %.

As described in Sects. 3.1–3.3, the error bars in Figs. 2–8 represent the minimum and the maximum PE observed for the actual analytical method, and thus are a measure of the method's variability. For the levoglucosan to ΣMA ratio the variability ranged from 0.9 to 13 % when including all laboratories. For the subselection of laboratories not influenced by outliers, the variability ranged from 0.9 to 4.8 %.

3.4.2 Mannosan to ΣMA ratio

The median theoretical relative contribution of mannosan to ΣMA ranged from 13–14 % for the laboratories from which this ratio could be derived; i.e., laboratories not affected by outliers of either of the three isomers or by levels below the detection limit. The mannosan to ΣMA ratio did not vary substantially between the laboratories included in the abovementioned subcategory. The largest difference was observed for filter sample 1 for which lab. 2 reported a value of 11 % and lab. 1 and 3 a value of 15 %. Lab. 7 reported values of levoglucosan for filter samples 1 and 2, which were considered outliers, hence, potentially affecting the ΣMA value and the mannosan to ΣMA ratio. The mannosan to ΣMA ratio for these two filter samples (16 %) did not differ substantially from that of filter samples 3–6 (13–16 %), while they were slightly higher compared to the subcategory not affected by outliers. Lab. 9 reported levels of galactosan for filter samples 1–6 which all were considered to be outliers; however, the mannosan to ΣMA

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ratio (14–17 %) did not experience a similar decrease as the levoglucosan to ΣMA ratio due to the substantially elevated concentrations of galactosan; on the contrary, they were in the upper range and above that seen for the subcategory not affected by outliers; i.e., the mean PE of 69 % seen for lab. 9 with respect to mannosan seems to have counteracted this.

The mean PE, representing the accuracy, ranged from −17 to 8 % for the various laboratories for which the mannosan to ΣMA could be derived (Fig. 6). Excluding lab. 9, which reported outliers for filter samples 1–6 with respect to galactosan, and lab. 7, which reported outliers for filters 1 and 2 for levoglucosan, did not have an influence on the reported range. Excluding the two outliers detected for lab. 7 improved the mean PE for the actual laboratory from 7.4 to 3.4 %.

As previously described, the error bars in Figs. 2–8 represent the minimum and the maximum PE observed for the actual analytical method, and thus are a measure of the method's variability. For the mannosan to ΣMA ratio the variability ranged from 2 to 20 % when including all laboratories. The range did not change for the subselection of laboratories not influenced by outliers.

3.4.3 Galactosan to ΣMA ratio

The median theoretical relative contribution of galactosan to ΣMA ranged from 3.9–5.0 % for the laboratories from which this ratio could be derived; i.e., laboratories not affected by outliers of either of the three isomers or by levels below the detection limit. The galactosan to ΣMA ratio varied more between laboratories than seen for the two other isomers considering the above mentioned subcategory. The largest difference was observed for filter sample 1 for which lab. 2 reported a value of 6.3 % and lab. 8 a value of 1.0 %. Lab. 7 reported values of levoglucosan for filter samples 1 and 2, which were considered outliers, hence, potentially affecting the ΣMA value and the galactosan to ΣMA ratio. The mannosan to ΣMA ratio for these two filter samples (3.5–3.6 %) was in the upper range of that seen for filter samples 3–6 (2.6–3.5 %), whereas they were slightly lower compared to the subcategory not affected by outliers. Lab. 9

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reported levels of galactosan for filter samples 1–6 which all were found to be outliers. The elevated levels reported by lab. 9 with respect to galactosan also had an effect on the galactosan to ΣMA ratio, which ranged from 17 to 27 %, being substantially higher than for the subcategory not affected by outliers.

The mean PE, representing the accuracy, ranged from −70 to 389 % for the various laboratories for which the galactosan to ΣMA could be derived (Fig. 7). Excluding lab. 9, which reported outliers for filter samples 1–6 with respect to galactosan, substantially narrowed the range (−70–45 %), whereas no change was observed when excluding lab. 7, which reported outliers for filter samples 1 and 2 for levoglucosan. Excluding the two outliers detected for lab. 7 changed the mean PE for the actual laboratory from −22 to −26 %. It should be noted that for lab. 8, the mean PE (−70 %) is based on filter samples 1 and 2 only, as galactosan for filter samples 3–6 was found to be below the detection limit.

The "error bars" in Figs. 2–8 represent the minimum and the maximum PE observed for the actual analytical method, and thus are a measure of the method's variability. For the galactosan to ΣMA ratio the variability ranged from 6 to 257 % when including all laboratories. The range was substantially narrowed (6–56 %) when excluding lab. 9, which reported outliers for filter samples 1–6 with respect to galactosan. Excluding lab. 7, which reported outliers for filter samples 1 and 2 for levoglucosan, did not have an effect on the total range.

3.5 The levoglucosan to mannosan ratio

The levoglucosan to mannosan ratio is occasionally used to apportion the amount of the residential wood burning emissions to burning of either soft- or hardwood (Caseiro et al., 2009; Favez et al., 2010; Piazzalunga et al., 2011; Maenhaut et al., 2012), with softwood combustion giving rise to low ratios (< 4) and hardwood to high ratios (14–15) (Schmidl et al., 2008). The latter authors proposed the following equation to derive the % spruce (or softwood) burnt (relative to the total amount of softwood + hardwood burnt):

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$$\%\text{spruce} = (14.8 - \text{levoglucosan/mannosan})/0.112 \quad (2)$$

where levoglucosan/mannosan is the levoglucosan to mannosan ratio in the ambient aerosol.

This equation was derived from data that were obtained for the combustion of common hardwood (beech and oak) and softwood species (spruce and larch) in wood stoves in Austria. Beside differences in the levoglucosan to mannosan ratio between various soft- and hardwood species, the uncertainty of the analytical methods used to quantify levoglucosan and mannosan is an unknown variable potentially contributing to the overall uncertainty when performing the soft- and hardwood attribution.

The median levoglucosan to mannosan ratio did not vary much between the six filter samples collected, ranging from 5.3–6.2 (Table B4), suggesting a rather stable composition of the wood burnt that impacted the sampling site. When comparing the laboratories from which this ratio could be extracted; i.e., laboratories not affected by outliers for either of the two isomers or by levels below the detection limit, the largest difference observed was seen for filter sample 5 for which lab. 2 reported a levoglucosan to mannosan ratio of 6.9 and lab. 9 a value of 3.6. Lab. 7 reported values of levoglucosan for filter samples 1 and 2, which were considered outliers, thus potentially affecting the levoglucosan to mannosan ratio. The levoglucosan to mannosan ratio for these two filter samples (4.9–5.0) was in the lower range of that of filter samples 3–6 (5.1–6.5), as well as being lower compared to the subcategory not affected by outliers.

The mean PE, representing the accuracy, ranged from −26 to 23 % for the various analytical methods from which the levoglucosan to mannosan ratio could be derived (Fig. 8). 78 % of the laboratories (lab. 3, 4, 6, 7, 8, 10, and 11) reported a mean PE for the levoglucosan to mannosan ratio within ±7 %, which should be considered quite a narrow range. Excluding the two outliers detected for lab. 7 changed the mean PE for the actual laboratory from −5.7 to −1.5 %, thus having no effect on the range including all laboratories.

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Assuming that the levoglucosan to mannosan ratio can thus be measured to within ±7 %, one can estimate the uncertainty from the analysis on the %spruce result derived from Eq. (2). This uncertainty is ±8 % spruce points for levoglucosan to mannosan ratios close to 14.8 % (thus for %spruce values close to 0 %) and gradually decreases to ±2 % spruce points for ratios close to 0 (%spruce values close to 100 %). However, the total uncertainty is likely much larger. It should be noted that besides MAs also other organic aerosol species, such as syringol and guaiacol, their derivatives, and retene, could be used to differentiate between hard- and softwood burning (e.g., Bari et al., 2009).

The "error bars" in Fig. 8 represent the minimum and the maximum PE observed for the actual analytical method, and thus the range can be considered a measure of the variability. For the levoglucosan to mannosan ratio the variability ranged from 3.5 to 24 %.

4 Conclusions

In the current study we have compared the results of thirteen different analytical methods used to quantify monosaccharide anhydrides (MAs) (i.e., levoglucosan, mannosan and galactosan) in ambient aerosol filter samples. To our knowledge, this is the first major intercomparison that has been conducted and reported in the scientific literature with respect to these compounds. All major methods used for analysis of MAs in ambient aerosol filter samples, and which have been reported in the scientific literature so far, are represented in the present intercomparison.

The results show that for levoglucosan the accuracy is only slightly lower than that reported for analysis of SO_4^{2-} on filter samples, a constituent that has been analyzed by numerous laboratories for several decades, typically by ion chromatography, and which should be considered a fairly easy constituent to analyze. Hence, the results obtained for levoglucosan with respect to accuracy are encouraging and suggest that levels of levoglucosan, and to a somewhat lesser extent for mannosan and galactosan, obtained

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by most analytical methods currently used to quantify monosaccharide anhydrides in ambient aerosol filter samples provide comparable results.

Finally, the various analytical methods used in the current study should be tested for other aerosol matrices and concentrations as well, the most obvious being summertime aerosol samples influenced by wild fires and/or agricultural fires.

Appendix A: Detailed description of analytical methods used for quantification of levoglucosan, mannosan and galactosan in the intercomparison

A1 HPAEC/Ion chromatography (IC)

Lab #2

For the analysis, punches of the filters (1 cm^2) were spiked with $^{13}C_6$-levoglucosan and extracted with 5 mL de-ionized water under 15 min gentle rotation. 50 µL of the filtered extracts (IC Acrodisc® syringe filter 0.45 µm Supor® (PES) membrane) were used for analysis. The MAs were measured using ion chromatography (Dionex IC-3000) coupled to a quadrupole mass spectrometer (Dionex MSQ). Separations were made using a Dionex CarboPac™ PA10 guard column (2 mm i.d. ×50 mm length) and a Dionex CarboPac™ PA10 analytical column (2 mm i.d. ×250 mm length), a 2 mm ASRS-300 suppressor, a CR-ATC anion trap column, and a potassium hydroxide eluent generator. Monosaccharide anhydrides were ionized using the ESI technique. The molecular ions of levoglucosan, mannosan and galactosan were monitored at m/z 161, whereas that of $^{13}C_6$-levoglucosan was monitored at m/z 167, using the selected ion mode. Levoglucosan was used for calibration.

Lab. #3

For the analysis, five punches of the filters with an area of 0.5 cm^2 each were eluted together with 5 mL Milli-Q grade water. Extraction was performed in polypropylene

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test tubes, which were first agitated with a Vortex and then put into an ultrasonic bath (20 min). After centrifugation (10 min) the aqueous extract was transferred into 4 micro centrifugation vials with 1 mL solution each. The solutions (injection volume 20 µL) were analyzed using ion chromatography with pulsed amperometric detection (HPAEC/PAD, ICS-3000 from Dionex Corp.). The separating column was a CarboPac MA1, the eluent concentration ranged from 0.48 M NaOH up to 0.65 M NaOH with a flow of 0.4 mL min^{-1}. Levoglucosan, mannosan and galactosan were identified by their retention time and quantified using external standards.

Lab #7

For the analysis, punches of the filters (1.6 cm^2) were extracted in 0.5 mL of Milli-Q grade water under ultrasonication for 30 min. The extract was filtered through a syringe filter (0.45 µm). The samples were analysed using a Dionex ICS-3000 system. The separation was carried out on a Dionex CarboPac MA1 column (4 × 250 mm) with a corresponding guard column (4 × 50 mm) at room temperature. The sample injection loop was 25 µL. The eluent gradient was programmed as follows: 0.52 M NaOH from 0 to 20 min, 0.52 M NaOH to 0.65 M NaOH in 15 min and held constant for 15 min. The eluent flow rate was 0.4 mL min^{-1}. The waveform used for pulsed amperometric detection was the standard quadruple potential for carbohydrate analysis. Levoglucosan, mannosan and galactosan were identified by their retention time and were quantified using external standards.

A2 HPLC

Lab. #1

For the analysis, punches (1.5 cm^2) of the filter were spiked with $^{13}C_6$-levoglucosan and $^{13}C_6$-galactosan and extracted twice with 2 mL tetrahydrofuran under ultrasonic agitation (30 min). The filtered extracts (Teflon syringe filter, 0.45 µm) were evaporated

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to a total volume of 1 mL in a nitrogen atmosphere. Before analysis the sample solvent elution strength was adapted to the mobile phase by adding Milli-Q water (0.8 mL). The concentrations of the MAs were determined using High-Performance Liquid Chromatography (HPLC) (Agilent model 1100) in combination with HRMS-TOF (high resolution time-of-flight mass spectrometry, Micromass model LCT) operated in the negative ESI mode. Levoglucosan, mannosan and galactosan were identified on the basis of retention time and mass spectra of authentic standards. Quantification was performed using isotope labeled standards of levoglucosan and galactosan. The mass traces at m/z 161.0455 and 167.0657 were used for quantification (approximately 50 mDa peak width).

Lab. #6

For the analysis, filters were spiked with $^{13}C_6$-levoglucosan and extracted 3 times with methanol in an ultrasonic bath for 30 min. The three extracts were pooled and evaporated to dryness. The sample was reconstituted with 1 mL methanol, shaken, and filtered through a nylon filter. The analysis was performed with liquid chromatography-mass spectrometry with ESI in the positive ionization mode. Sodium acetate 2 mM was added to the LC mobile phase to form sodium adducts of levoglucosan and mannosan. The analytes were separated by a gradient using 10 mM sodium acetate and methanol as mobile phase. The LC column was a Benson Polymeric BP-100 Ca++ Carbohydrate Column. Analysis was performed in the selected ion monitoring (SIM) of the Na adducts. The ion monitored for levoglucosan and mannosan was m/z 185, whereas that for $^{13}C_6$-levoglucosan was m/z 191.

Lab. #8

For the analysis, filter punches (4.5 cm^2) were extracted with 2 mL ultrapure water by 30 min vortex agitation. 449 µL of the filtered extracts (Acrodisc syringe filters, 0.2 µm) were analyzed by liquid chromatography (Dionex DX500) electrospray

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ionization–tandem mass spectrometry (Thermo Fisher Scientific LCQ Fleet). Levoglucosan, mannosan and galactosan were identified and quantified on the basis of retention time and specific multiple reaction monitoring (MRM) transition (m/z 161–113 for levoglucosan and galactosan, m/z 161–101 for mannosan). External calibrations were performed using standards of levoglucosan, mannosan, and galactosan.

Lab. #10

For the analysis, the entire filter punch was extracted twice with 6 mL pure water in an ultrasonic bath for 45 min. Extracts were filtered (Teflon syringe filter, 0.2 µm) and 50 µL of chloroform were added to prevent from bacteria activity. Extracts were kept frozen (−18 °C) until analysis. The analyses were performed using an ultra-performance liquid chromatography (UPLC, Waters) instrument coupled with a triple quadrupole mass spectrometer (Applied Biosystems, model API3200). Separation of MAs was achieved using an Acquity UPLC HSS T3 column, a sample loop of 10 µL, a mixed water-methanol solvent, and post-column addition of methanol. Levoglucosan, mannosan and galactosan were identified and quantified on the basis of retention time and specific MRM transition (m/z 161–113 for levoglucosan and galactosan, m/z 161–113 for mannosan). External calibrations were performed using standards.

A3 GC

Lab. #4

For the GC/MS analyses, 3 filter punches (1 cm^2 each) were spiked with recovery standard (methyl *O*-L-xylanopyranoside). Each punch was extracted three times with 10 mL methanol for 5 min under ultrasonic agitation. The combined extract was reduced in volume with a rotary evaporator to about 1 mL. The filtered concentrate (Teflon syringe filter, 0.45 µm) was completely dried under a stream of nitrogen. 40 µL of BSTFA + 1 % TMCS/pyridine (2/1) was added to the dried sample, and the mixture reacted at 70 °C

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for 1 h. An aliquot of 1 µL was immediately analyzed by GC/MS (Thermo-Finnigan, TRACE GC2000 and Polaris Q). Quantification of the MAs was performed in the scanning mode (m/z 45–650) from the total ion chromatogram using relative response factors determined by injection of authentic standards of levoglucosan, galactosan, and mannosan.

Lab. #5

For the GC/MS analyses, 3 to 4 filter punches (0.79 cm^2 each) were spiked with internal standard. Each sample was extracted twice with 8 mL dichloromethane/methanol mixture (4/1) for 30 min in ultrasonic bath. The filtered extracts (Teflon syringe filter, 0.45 µm) were evaporated to dryness under a gentle flow of nitrogen. 70 µL BSTFA and 70 µL pyridine were added to derivatise the analytes. The mixtures were reacted at 70 °C for 3 h. 1 µL of the sample was injected into the GC injector (Agilent 6890N) in the splitless mode. The EI ionization mass spectrometer with quadrupole mass analyzer (Agilent 5973) was operated in the SIM mode, the acquisition frequency was 2.74 cycles s^{-1}. The ion at m/z 333 was used for the evaluation. Calibration was performed with a standard solution of levoglucosan.

Lab. #9

In the GC/MS method, punches (0.85 or 1.0 cm^2) of the samples were spiked with internal standard $^2H_7$-levoglucosan and ultrasonically extracted twice with 5 mL of a mixture of dichloromethane/methanol (2/1) for 15 min under ultrasonic agitation, each. The filtered extracts (glass fiber filters, 0.60 mm) were concentrated in a rotary evaporator to a small volume (ca. 200 µL), and then to dryness under a nitrogen flow. 50 µL BSTFA +1 % TMCS was added and maintained at 70 °C for 3 h. After derivatization, the excess of derivatization agent was evaporated by a nitrogen flow and hexane was added to obtain a volume of 0.5 mL. The concentrations were determined using PTV-GC (Thermo-Finnigan, Trace GC) in combination with a MS detector

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(Thermo-Finnigan, Polaris-Q). 10 µL of sample was injected and p-terphenyl was used as recovery standard. The chromatograms were acquired in the full scan mode (m/z 50–500). Compounds were quantified according to their characteristic ion: levoglucosan (m/z 204); mannosan and galactosan (m/z 217). Quantification was performed using isotope-labeled $^{2}H_{7}$-levoglucosan (m/z 220).

Lab. #11

For the GC/MS analyses, samples were divided into two parts (2.27 cm^2 and rest of the filter). Sedoheptulose was added as internal standard and filters were extracted by refluxing with 300 mL dichloromethane/methanol (2/1) for 24 h. The filtered extracts (glass filtration unit, 0.45 µm) were concentrated in a rotary evaporator to a volume of about 2 mL, transferred to a vial, and evaporated to dryness under a nitrogen stream. The dried extracts were redissolved in pyridine (100 µL) and derivatized with 200 µL BSTFA +1 % TMCS at 70 °C for 3 h. For quantification 1 µL of the reaction mixture was injected. The concentrations of MAs were determined by gas chromatography (Agilent 6890) mass spectrometry (Agilent 7873). Levoglucosan was identified on the basis of retention time and mass spectra of an authentic standard. Quantification of the three anhydrosugars was performed in the scanning mode using relative response factors determined by injection of levoglucosan standard.

Lab. #12

Analyses were carried out using in-situ derivatization thermal desorption gas chromatography time of flight mass spectrometry (IDTD-GC-TOFMS). Filter punches (0.12–0.28 cm^2) were placed into a GC-liner, internal standard ($^{13}C_6$-levoglucosan) was added, and liners were closed. For derivatization filter punches were soaked with 10 µL MSTFA. Closed liners were placed in an oven at 80 °C for 1 h. After this derivatization step the liners were put into the cold injector. For desorption, the temperature was raised to 300 °C and kept for 16 min. During desorption MSTFA was added to the

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carrier gas. Analytes were focused on a retention gap at 70 °C followed by GC separation (Agilent 6890). The TOFMS instrument (Leco Pegasus III) was operated at a data acquisition frequency of 25 scans s^{-1}. The mass range was m/z 30–500. For quantification m/z 333 for tris-trimethylsilyl-levoglucosan and m/z 338 for tris-trimethylsilyl-$^{13}C_6$-levoglucosan were used. External calibration was done with native levoglucosan.

Lab. # 13

For the GC/MS analyses, filter punches (1 cm^2) were extracted 3 times (15, 10, 5 mL) with a mixture of dichloromethane/methanol (3/1) and subjected to ultrasonic agitation (45, 30, 15 min). The filtered extracts (Teflon syringe filter, 0.45 µm) were evaporated to dryness in a nitrogen stream. The dry mass was re-dissolved in 1 mL of dichloromethane. 50 µL of each extract solution and 5 µL of 1,4-dithioerythritol solution (0.5 µg mL^{-1}) were evaporated to dryness under a stream of nitrogen at 60 °C. 30 µL pyridine and 10 µL of MSTFA + 1 % TMCS were added, and the mixture reacted at 80 °C for 1 h. The solution was evaporated to dryness at 60 °C under a continuous flow of nitrogen. The dry mass was dissolved in 50 µL of dichloromethane containing 1-phenyldodecane (5 µg mL^{-1}). For quantification 2 µL were injected. The concentrations of the anhydrosugars were determined by gas chromatography (Agilent 6890) mass spectrometry (Agilent 5973). Levoglucosan was identified on the basis of retention time and mass spectrum of authentic standard. Quantification was performed using the selective ion monitoring mode. Compounds were quantified according to their characteristic m/z 217 and 204 for levoglucosan and m/z 246 for 1-phenyldodecane.

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Table 1. Overview and short description of the analytical methods used by the participating laboratories in the present intercomparison, including the method's capability for isomer separation, the method's limit of detection (LOD), the instrument used for separation and detection of the analytes, the solvent(s) used for extraction, and whether derivatization of the analytes was applied.

Lab no.	Isomer separation	LOD* (ng m^{-3})	Instrument	Solvent	Derivatization
#1	Yes	0.28	HPLC/HRMS-TOF (ESI−)	tetrahydrofuran	No
#2	Yes	2.2	IC/QMS (ESI−)	deionized H_2O	No
#3	Yes	5.0	HPAEC/PAD	deionized H_2O	No
#4	Yes	0.05	GC/MS	methanol	Yes
#5	No	0.05	GC/QMS	dichloromethane/methanol	Yes
#6	Yes	1.8	LC/MS (ESI+)	methanol	No
#7	Yes	0.004	HPAEC/PAD	deionized H_2O	No
#8	Yes	3.0	LC/MS-MS (ESI−)	deionized H_2O	No
#9	Yes	0.02	GC/MS	dichloromethane/methanol	Yes
#10	Yes	0.19	UPLC/MS-MS	deionized H_2O/methanol	No
#11	Yes	0.02	GC/MS	dichloromethane/methanol	Yes
#12	Yes	0.004	TD-GC-TOFMS	none	Yes
#13	Yes	0.05	GC-QMS	dichloromethane/methanol	Yes

* LOD calculated for an air volume of 2.3 m^3 h^{-1} for 24 h and an exposed filter area of 12 cm.

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Table B1. Summarized description of the analytical methods used by the participating laboratories in the present intercomparison, including extraction procedure, derivatization agent, recovery standard, and quantification standards.

Lab number	Separation	Detection	Extraction	Derivatization agent	Internal std./Recovery std.	Quantification standard(s)
#2	IC	QMS	H_2O, Shaking	–	$^{13}C_6$-levoglucosan (98 %)	levoglucosan (99 %), mannosan (98 %), galactosan (n.g.)
#3	IC	Pulsed amperometric	H_2O, Ultrasonic agitation	–	–	levoglucosan (99 %), mannosan (98 %), galactosan (n.g.)
#7	IC	Pulsed amperometric	H_2O, Ultrasonic agitation	–	–	levoglucosan (> 98 %), mannosan (> 98 %), galactosan (n.g.)
#1	HPLC	HR-TOFMS	THF, Ultrasonic agitation	–	$^{13}C_6$-levoglucosan (98 %), $^{13}C_6$-galactosan (98 %)	levoglucosan (99 %), mannosan (98 %), galactosan (n.g.)
#6	HPLC	QMS	MeOH, Ultrasonic agitation	–	$^{13}C_6$-levoglucosan (98 %)	levoglucosan (98 %), mannosan (98 %)
#8	HPLC	MS/MS	H_2O, Vortex	–	–	levoglucosan (99 %), mannosan (n.g.), galactosan (n.g.)
#10	UPLC	MS/MS	H_2O, Ultrasonic agitation	–	–	levoglucosan (99 %), mannosan (n.g.), galactosan (n.g.)
#4	GC	ITMS	MeOH, Ultrasonic agitation	pyridine, BSTFA +1 % TMCS	*O*-L-xylanopyranoside (99 %)	levoglucosan (99 %), mannosan (98 %), galactosan (n.g.)
#5	GC	QMS	DCM/MeOH, Ultrasonic agitation	pyridine, BSTFA	succinic acid-$^2H_4$ (98 %)	levoglucosan (99 %)
#9	GC	ITMS	DCM/MeOH, Ultrasonic agitation	BSTFA +1 % TMCS	levoglucosan-$^2H_7$ (n.g.)/ *p*-terphenyl (99 %)	levoglucosan (99 %), mannosan (n.g.), galactosan (98 %)
#11	GC	QMS	DCM/MeOH, Soxhlet	pyridine, BSTFA +1 % TMCS	sedoheptulose (> 99 %)	levoglucosan (99 %)
#12	GC	TOFMS	Thermal desorption	MSTFA (in situ)	$^{13}C_6$-levoglucosan (99 %)	levoglucosan (99 %)
#13	GC	QMS	DCM/MeOH, Ultrasonic agitation	pyridine, MSTFA +1 % TMCS	1-phenyldodecane (99 %)	levoglucosan (99 %), galactosan (99 %)

n.g.: not given.

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Table B2. Results of the homogeneity test of the six filter samples subjected to the present intercomparison. The results were obtained from one 1.0 cm^2 punch taken from each of the 16 sectors pr filter; i.e., a total of 96 analyses were performed for each of the three isomers. The filter samples were analyzed according to the method described in Appendix A.

	Filter sample 1	Filter sample 2	Filter sample 3	Filter sample 4	Filter sample 5	Filter sample 6
Levoglucosan						
Mean ± SD (ng cm^{-2})	1518 ± 179	1403 ± 127	604 ± 99	440 ± 48	541 ± 51	456 ± 48
Median (ng cm^{-2})	1478	1434	631	435	537	445
Mean/Median	1.03	0.98	0.96	1.01	1.01	1.03
RSD (%)	12	9.1	16	11	9.5	10
Outlier	–	–	–	–	–	–
Mannosan						
Mean ± SD (ng cm^{-2})	446 ± 46	370 ± 46	87 ± 22	75 ± 26	103 ± 20	86 ± 9
Median (ng cm^{-2})	437	366	93	77	109	85
Mean/Median	1.02	1.01	0.93	0.98	0.95	1.01
RSD (%)	10	12	26	35	19	10
Outlier	–	–	–	–	1	–
Galactosan						
Mean ± SD (ng cm^{-2})	112 ± 15	98 ± 11	21 ± 9.5	19 ± 7.8	34 ± 5.2	26 ± 3.9
Median (ng cm^{-2})	107	96	21	16	34	26
Mean/Median	1.04	1.02	0.99	1.13	1.00	1.02
RSD (%)	13	11	45	42	15	15
Outlier				1	1	

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Table B3. Calculated mean (± SD) and median concentrations, as well as maximum and minimum concentrations of levoglucosan, mannosan and galactosan in the six filter samples subjected to the intercomparison, as obtained by the various methods applied. Number of values included in the calculated concentrations, outliers and values below the detection limit (BDL) are listed. Outliers and values BDL are not included in the calculated concentrations, nor in the listed maximum and minimum values.

Sample code	Isomer	Mean ± SD (ng cm^{-2})	Median	Max	Min	*n*	Outliers	BDL
Filter 1	Levoglucosan	1730 ± 302	1765	2190	965	12	1 (lab. #7)	
	Mannosan	275 ± 122	300	489	68	9		
	Galactosan	76 ± 40	90	124	11	8	1 (lab. #9)	
Filter 2	Levoglucosan	1592 ± 317	1631	2132	873	12	1 (lab. #7)	
	Mannosan	256 ± 105	263	441	65	9		
	Galactosan	68 ± 34	79	101	14	8	1 (lab. #9)	
Filter 3	Levoglucosan	594 ± 141	627	765	280	13		
	Mannosan	101 ± 37	99	166	47	9		
	Galactosan	39 ± 18	40	68	12	6	1 (lab. #9)	2 (lab. #3, #8)
Filter 4	Levoglucosan	544 ± 123	570	678	268	13		
	Mannosan	87 ± 33	80	146	42	9		
	Galactosan	37 ± 20	33	71	11	6	1 (lab. #9)	2 (lab. #3, #8)
Filter 5	Levoglucosan	566 ± 134	586	758	258	13		
	Mannosan	110 ± 45	110	188	45	9		
	Galactosan	36 ± 20	35	70	11	6	1 (lab. #9)	2 (lab. #3, #8)
Filter 6	Levoglucosan	521 ± 122	552	670	270	13		
	Mannosan	99 ± 36	100	162	51	9		
	Galactosan	35 ± 20	31	68	9	6	1 (lab. #9)	2 (lab. #3, #8)

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Table B4. Calculated mean (±SD) and median ratios, as well as maximum and minimum ratios of levoglucosan, mannosan and galactosan to the sum of the three isomers (ΣMAs), as well as the mannosan to levoglucosan ratio in the six filter samples subjected to the intercomparison, as obtained by the various methods applied. Number of values included in the calculated values are listed. Outliers and values BDL are not included in the calculated concentrations, nor in the listed maximum and minimum values.

Sample code	Isomer	Mean ± SD	Median	Max	Min	*n*
Filter 1	Levo/ΣMA (%)	82 ± 2.1	82	87	81	6
	Manno/ΣMA (%)	14 ± 1.4	14	15	11	6
	Galacto/ΣMA (%)	4.0 ± 1.7	4.2	6.3	1.0	6
	Levo/Manno	5.9 ± 0.9	5.8	7.2	4.5	8
Filter 2	Levo/ΣMA (%)	82 ± 1.2	83	83	80	6
	Manno/ΣMA (%)	14 ± 1.4	14	15	12	6
	Galacto/ΣMA (%)	3.8 ± 1.4	3.9	5.5	1.4	6
	Levo/Manno	5.8 ± 0.7	5.7	7.1	4.9	8
Filter 3	Levo/ΣMA (%)	82 ± 0.7	82	83	81	5
	Manno/ΣMA (%)	13 ± 1.2	13	14	11	5
	Galacto/ΣMA (%)	4.7 ± 0.9	5.0	5.8	3.5	5
	Levo/Manno	6.0 ± 1.0	6.0	7.5	4.5	9
Filter 4	Levo/ΣMA (%)	82 ± 0.8	82	84	82	5
	Manno/ΣMA (%)	13 ± 1.2	13	14	11	5
	Galacto/ΣMA (%)	4.8 ± 0.9	4.7	6.3	3.4	5
	Levo/Manno	6.2 ± 1.1	6.4	7.7	4.6	9
Filter 5	Levo/ΣMA (%)	81 ± 0.8	82	82	80	5
	Manno/ΣMA (%)	14 ± 1.5	14	16	12	5
	Galacto/ΣMA (%)	4.3 ± 1.0	4.0	6.1	3.4	5
	Levo/Manno	5.3 ± 1.0	5.7	6.9	3.6	9
Filter 6	Levo/ΣMA (%)	81 ± 0.6	81	82	80	5
	Manno/ΣMA (%)	14 ± 1.5	14	16	12	5
	Galacto/ΣMA (%)	4.4 ± 1.5	4.0	6.8	2.6	5
	Levo/Manno	5.3 ± 0.9	5.6	6.7	3.8	9

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Table C1. Abbreviations used.

ACD	Aerosol charge detection
BB	Biomass burning
BSTFA	*N*,*O*-Bis(trimethylsilyl)trifluoroacetamide
CE	Capillary electrophoresis
DCM	Dichloromethane
ESI	Electrospray ionization
GC	Gas chromatography
HPAEC	High-performance anion-exchange chromatography
HPLC	High-performance liquid chromatography
HR-TOFMS	High-resolution time-of-flight mass spectrometry
ITMS	Ion trap mass spectrometry
MAs	Monosaccharide anhydrides
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
MSTFA	*N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide
MeOH	Methanol
PAD	Pulsed amperometric detection
PM	Particulate matter
QMS	Quadrupole mass spectrometry
THF	Tetrahydrofuran
TOFMS	Time-of-flight mass spectrometry
TMCS	Chlorotrimethylsilane
UPLC	Ultra-performance liquid chromatography

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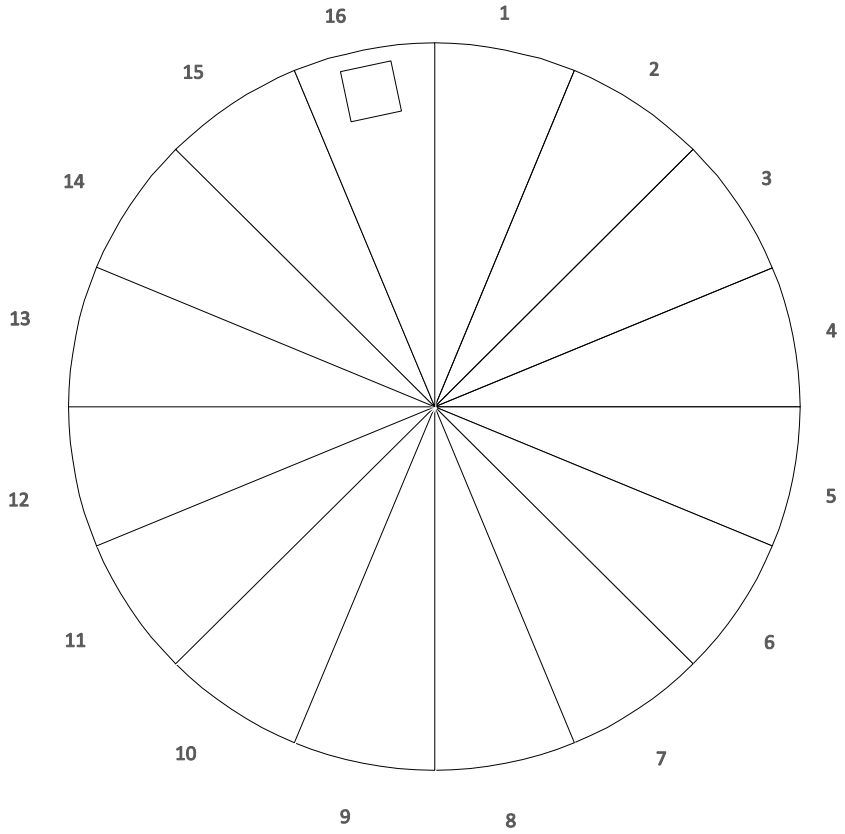

Figure 1. Schematic drawing illustrating the subdivision of one of the six filter samples subjected to the intercomparison. The square in sector 16 illustrates the 1.0 cm^2 punch taken from each of the 16 sectors pr. filter sample to perform a homogeneity test of the filter samples. Each of the sectors sent out to the participating laboratories had an exposed filter area of 8.6 cm^2; i.e., when accounting for the removal of the 1.0 cm^2 punch.

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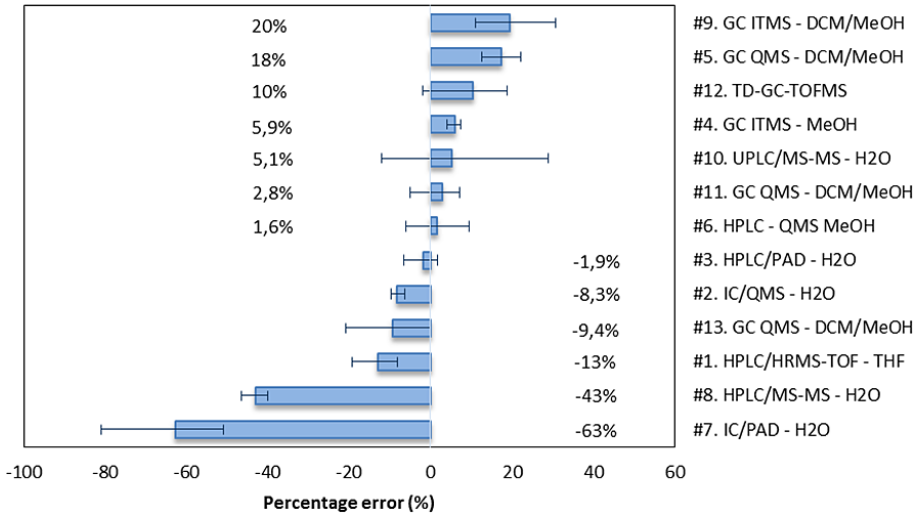

Figure 2. Calculated mean percentage error (PE) for each of the thirteen laboratories reporting levels of levoglucosan in the current intercomparison. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right of the figure.

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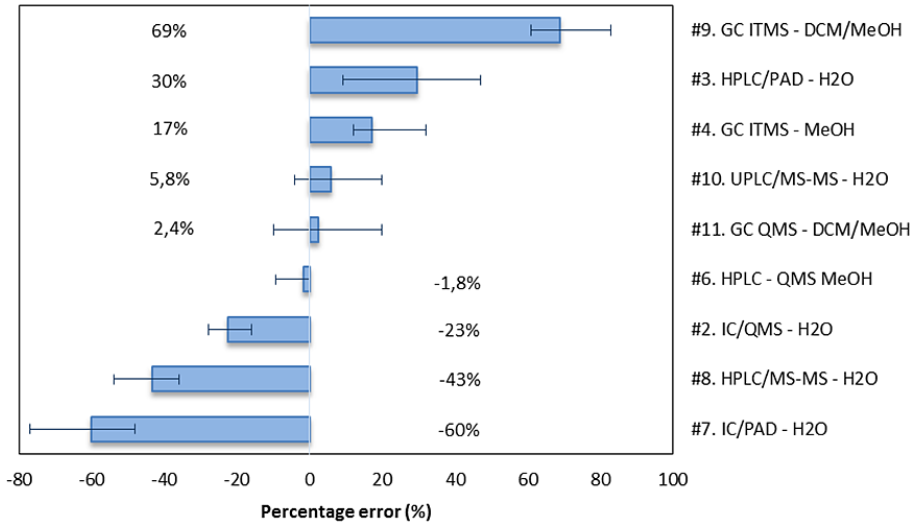

Figure 3. Calculated mean percentage error (PE) for each of the nine laboratories reporting levels of mannosan in the current intercomparison. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right of the figure.

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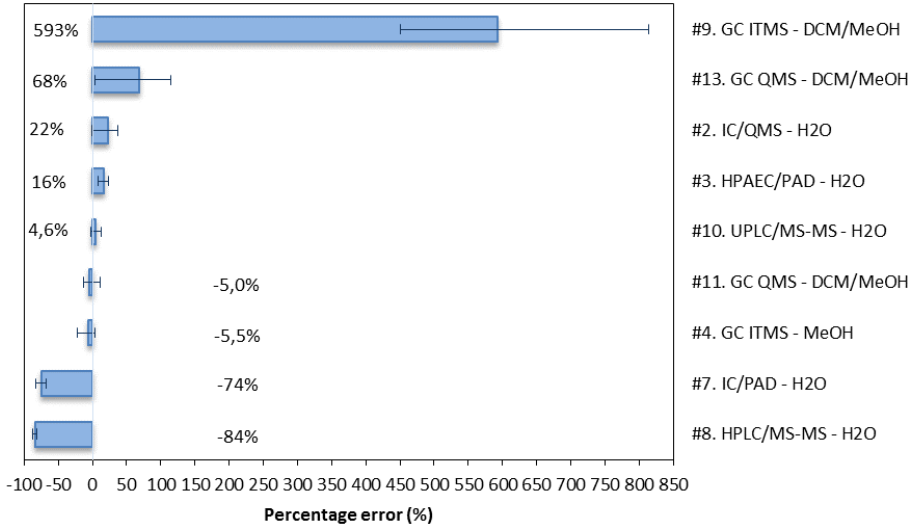

Figure 4. Calculated mean percentage error (PE) for each of the nine laboratories reporting levels of galactosan in the current intercomparison. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all of the six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right in the figure.

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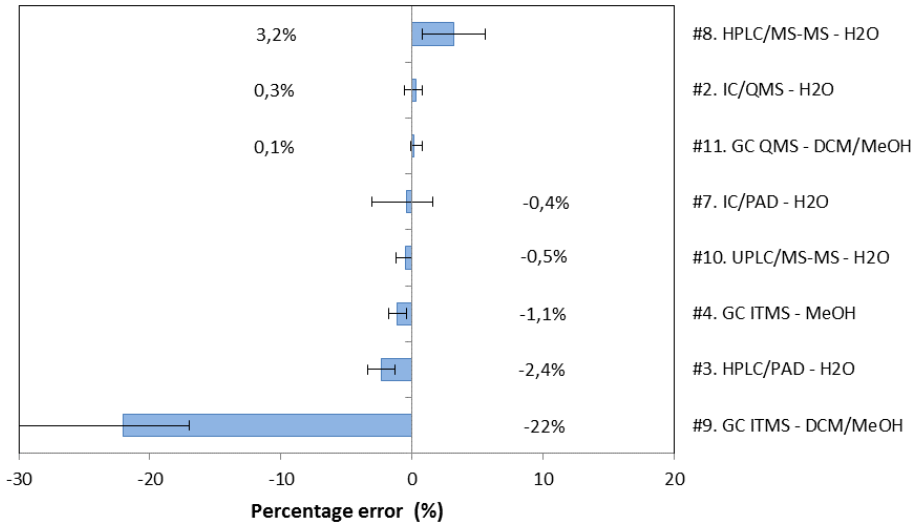

Figure 5. Calculated mean percentage error (PE) for each of the eight laboratories for which the levoglucosan to ΣMA ratio could be derived. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all of the six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for are mentioned at the right of the figure.

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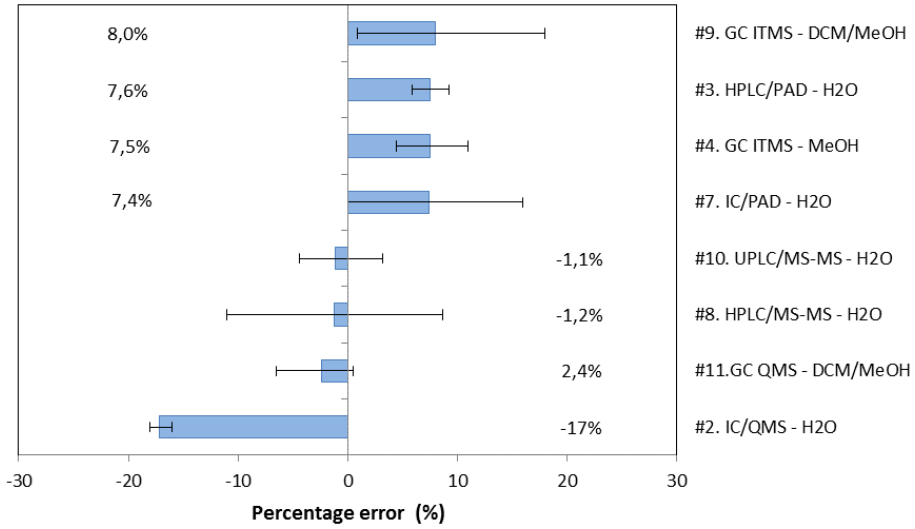

Figure 6. Calculated mean percentage error (PE) for each of the eight laboratories for which the mannosan to ΣMA ratio could be derived. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all of the six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right of the figure.

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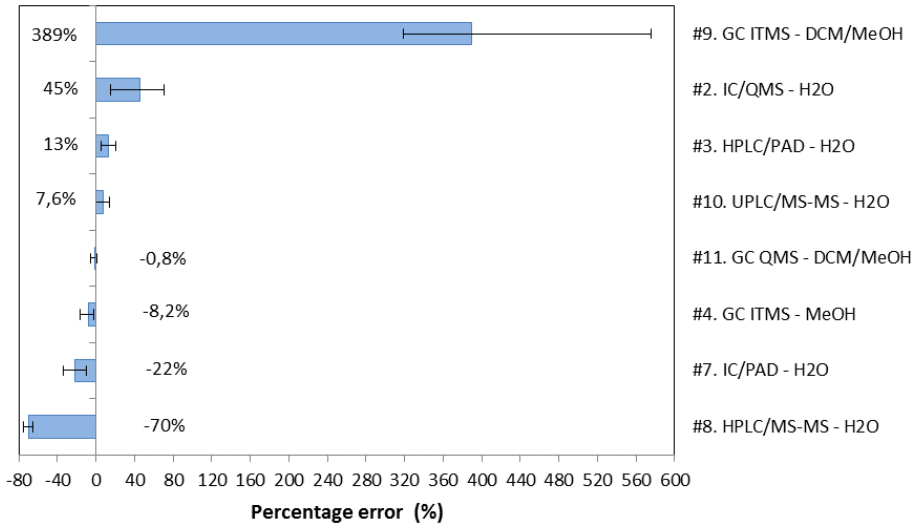

Figure 7. Calculated mean percentage error (PE) for each of the eight laboratories for which the galactosan to ΣMA ratio could be derived. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right of the figure.

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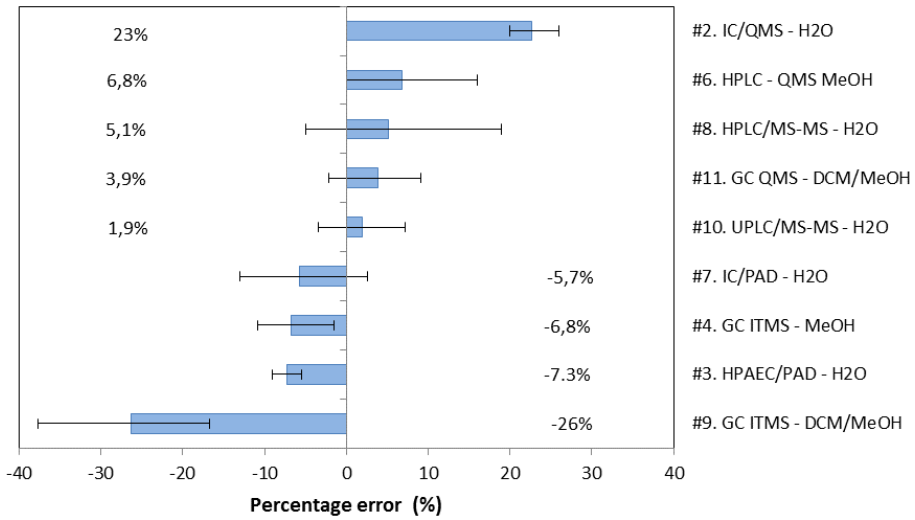

Figure 8. Calculated mean percentage error (PE) for each of the nine laboratories for which the levoglucosan to mannosan ratio could be derived. The PE was calculated according to Eq. (1) (Sect. 2.5) for each of the six sectors received by the participating laboratories. The mean PE for each laboratory accounts for the PE calculated for all of the six sectors. The laboratory number, ranging from 1–13, the analytical method and solvent used for extraction are mentioned at the right of the figure.

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