Determination of levoglucosan and its isomers in size fractions of aerosol standard reference materials

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ABSTRACT

The present study tested the extraction efficiency and quantification reproducibility of anhydrosugars in a series of NIST SRMs using two extraction protocols and isotopically-labeled (d7-levoglucosan) vs. chemically analogous (sedoheptulosan) surrogates. In both instances, levoglucosan concentrations in the different versions of the Washington, D.C. urban dust standard (SRM 1649, 1649a, 1649b, and RM 8785) were similar. The present test also showed that levoglucosan concentrations were not affected by long-term shelf storage of dry material. Variability of analyses were similar for both surrogates and averaged -5%. Surrogate recoveries were shown to average 103 ± 7% and 97 ± 7% for d7-levoglucosan and sedoheptulosan, respectively. The choice of solvent was shown to affect recoveries the most (but not variability). Levoglucosan concentrations were either seriously underestimated or overestimated with ethyl acetate extraction when d7-levoglucosan or sedoheptulosan was used as surrogate, respectively. These results point to the need to use some fraction of polar solvent (i.e. methanol) in the solvent mixture. Anhydrosugar concentrations in the urban dust from the Czech Republic (candidate SRMs 2786 and 2787) were characterized by 3- to 7-fold higher anhydrosugar concentrations than those observed in the Washington, D.C. urban dust. The internal anhydrosugar signatures (i.e. levoglucosan/mannosan ratio: L/M) confirm the predominance of biomass combustion sources in both SRM series with mixed inputs from hardwood and softwood combustion in the Washington, D.C. urban dust and a predominantly softwood source in the Prague urban dust. The uniform distribution of anhydrosugars, across the particle size distribution of both SRM series, confirms earlier studies that low temperature charred materials contribute significant inputs to atmospheric ultrafine particles with long atmospheric residence time and transport ranges.

1. Introduction

Levoglucosan (1,6-anhydro-β-D-glucopyranose) and its isomers (mannosan and galactosan) are dehydro-monomosaccharide derivatives formed exclusively from the thermal breakdown of cellulose and hemicellulose, respectively, during combustion. As such, they are source specific and should hypothetically be found in residues of incomplete combustion of fuels containing cellulose/hemicellulose (Shafizadeh et al., 1979; Simoneit et al., 1999; Simoneit, 2002; Otto et al., 2006; Fabbri et al., 2008a; Kuo et al., 2008a; Schmidl et al., 2008). Simoneit et al. (1999) were among the first to show that levoglucosan and related degradation products from cellulose could be utilized as specific indicators for the presence of emissions from biomass burning in samples of atmospheric fine particulate matter (PM). Since that work, a large number of studies have used of levoglucosan as a qualitative marker of biomass combustion in atmospheric particles (Nolte et al., 2002; Oros et al., 2002; Fraser et al., 2003; bin Abas et al., 2004a;b; Fine et al., 2004; Simoneit et al., 2004b; Ward et al., 2006; Schmidl et al., 2008; Engling et al., 2009) and in some cases as a tracer allowing quantitative apportionment of biomass combustion in the atmosphere at the local to regional scale (Fraser and Lakshmanan, 2000; Zdrahal et al., 2002; Jordan et al., 2006; Lee et al., 2008; Caseiro et al., 2009). Detailed characterization of the proportional yield of levoglucosan to its isomers and particularly to mannosan in fuel source emissions has further permitted discrimination between specific inputs of combustion (i.e. softwood vs. hardwood, brown coal vs. recent
biomass) in atmospheric PM (Ward et al., 2006; Schmidl et al., 2008; Caseiro et al., 2009; Engling et al., 2009; Fabbrì et al., 2009). Additional works have also started to use this biomarker as a tool for black carbon characterization (Kuo et al., 2008a), paleofire reconstructions (Elías et al., 2001; Hunsinger et al., 2008), as well as human exposure to biomass combustion (Migliaccio et al., 2009).

Despite this wide-ranging series of studies, there is still a dearth of materials that can be used for method validation (i.e. reference materials with certified levoglucosan values) or even an extraction protocol that ensures quantitative recoveries of anhydrosugars from particulate matter. Most methodological studies dealing with levoglucosan have focused on detection approaches (i.e. GC/MS and GC/MS–MS) in order to optimize sensitivity and selectivity (Pashynska et al., 2002) or increase throughput using simplified extraction/quantitation methods (García et al., 2005; Schkolnik and Rudich, 2006; Ward et al., 2006). Few have sought to establish a protocol including control materials to validate extraction recovery and quantitation accuracy. Recently, Simpson et al. (2004) documented recoveries of levoglucosan from diverse spiked filter media (PTFE, quartz, and Zellfluor) and using ethyl acetate as the extraction solvent. They reported that recoveries of levoglucosan and its surrogate (sedoheptulosan) varied depending on the filter used (69–90%, respectively) and that ethyl acetate was not appropriate for extraction of the more polar surrogate when hydrogen bonding interactions occurred with the matrix. Similarly, Fabbrì et al. (2008b) demonstrated that extraction efficiency from spiked filters was highly dependent on both the polarity of the solvent mixture and the filter matrix (reflon, quartz, glass) with sedoheptulosan showing the lowest recovery from glass fiber filters. An additional recent study by Larsen et al. (2006) tested a series of NIST Standard Reference Materials (SRMs) using a suite of different extraction protocols. Discrepancies, however, exist between the data presented by Larsen et al. (2006) and Kuo et al. (2008a) for the same material. The goals of this study were a) to systematically test the extraction efficiency and the reproducibility of anhydrosugar quantification in homogeneous atmospheric PM using previously cited extraction protocols (Larsen et al., 2006; Kuo et al., 2008a), and b) to evaluate potential differences/similarities in anhydrosugar distribution across different particle size fractions of these SRMs.

2. Experimental

2.1. General description of the materials used

Two series of atmospheric aerosols used were prepared by the U.S. National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA). Both were collected in urban settings and are thus also referred to as urban dust SRMs. The first urban dust was collected in 1976–1977 in the Washington, D.C. area over a period in excess of twelve months and thus represents a time-integrated sample for that period. The material was then sieved through a fine-mesh sieve (\(<125 \ \mu m\)) and issued as SRM 1649 in 1982 as a standard for polymeric aromatic hydrocarbon analyses in aerosols. This material was re-certified in 1999 for additional organic and inorganic contaminants as well as radiocarbon and total organic carbon content and issued as SRM 1649a. A re-certification of this material was recently performed after first sieving it to pass through a 63 \(\mu m\) sieve (SRM 1649b). Finally, an ultrafine separation (\(<2.5 \ \mu m\)) of the Washington, D.C. particulate matter was also performed and made available as reference material (RM) 8785. An additional urban aerosol was recently collected over a 1-year collection cycle from spring 2004 to spring 2005 in Prague, Czech Republic. The bulk particulate matter was homogenized and then size fractionated to nominally represent the \(<4 \ \mu m\) fraction (candidate SRM 2786) and the \(<10 \ \mu m\) fraction (candidate SRM 2787).

Several vials of urban dust (SRM 1649a) were purchased from NIST from 2005 to 2006. From the moment of their purchase, these standards were preserved in a desiccator at room temperature. Dr. Eric Crevelius (Pacific Northwest National Laboratory, WA) kindly provided a vial of the prior version of urban dust (SRM 1649). This standard was purchased in 1995 and stored on a shelf at room temperature. In addition, a new version of the urban dust (SRM 1649b) was provided by NIST to perform a comparative analysis between this smaller size fraction (\(<63 \ \mu m\)) and the original bulk material. The urban dust particulates from the Czech Republic were also provided by NIST to compare anhydrosugar concentrations in standardized atmospheric particulates from a region of the world known for its high atmospheric PM loads (Bridgman et al., 2002; Branis and Domasova, 2003).

2.2. Analytical procedures

All materials were extracted (30 ± 5 mg) using the method described in Kuo et al. (2008a) with slight modifications. Samples were extracted via pressurized fluid extraction (PFE) with an accelerated solvent extractor (Dionex ASE 200) at 10.3 MPa and 100°C. Replicate extractions were performed over ~9 months in two different laboratories using similar ASE instruments. Prior to extraction, the samples were spiked with the surrogate standard sedoheptulosan (Sigma, MO, USA; Simpson et al., 2004) and/or \(d_2\)-levoglucosan (NIST SRM 2267; Larsen et al., 2006). The majority of samples were extracted using a mixture of dichloromethane and methanol (DCM:MeOH: 9:1, v/v) as described in Kuo et al. (2008a). For comparative purposes, however, a few aliquots of SRMs 1649a and 1649b were extracted using 100% ethyl acetate (EA) according to the extraction protocol described in Larsen et al. (2006). The extracts were evaporated to dryness using a LabConco™ solvent concentrator. Samples were redissolved in 700 \(\mu L\) pyridine. An aliquot (75 \(\mu L\)) was transferred to a 1.5 mL glass vial to which 75 \(\mu L\) of \(N,O\)-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS; Supelco, PA, USA) was added. The samples were derivatized under normal atmosphere by heating at 75°C for 1 h in a 20-wells block heater. After derivatization, each sample was transferred to a 250 \(\mu L\) glass autosampler vial insert to which 50 \(\mu L\) of triisopropylbenzene (Aldrich, MO, USA; Simpson et al., 2004) was added to serve as a GC-internal standard.

All analyses were performed using gas chromatography-mass spectrometry (GC/MS) with a Varian Ion Trap 3800/4000 system fitted with a fused silica column (VF 5MS, 30 m, 0.25 mm i.d., 0.25 \(\mu m\) film; Varian Inc.). Each sample was injected, under splitless mode, into a straight glass liner inserted into the GC injection port; helium was used as the carrier gas (1.0 mL min \(^{-1}\)). The GC oven was programmed from 65°C (2 min) to 300°C (5 min) at 6°C min \(^{-1}\). The GC injector and GC/MS interface were both maintained at 270°C. The mass spectrometer was operated in the electron ionization (EI, 70 eV) and full scan modes. Data were acquired and processed with the Varian MS Workstation software (version 6.6). Compound identification was performed using GC retention times and by comparing full mass spectra with those of commercially available standards (levoglucosan, 99%, Aldrich, St. Louis, MO, USA). Quantification was performed using relative response factors (RRF) adjusted to the surrogate standard and determined using multiple injections (n = 6) of a one-point calibration curve. The standard deviation of the RRF was less than 2% and corresponded to that determined with a 5-points calibration curve (Kuo et al., 2008a). The method detection limit (MDL), determined as 3 times the standard deviation of 7 low concentration standard spike replicates, was 0.021, 0.030, and 0.038 ng mL \(^{-1}\) for levoglucosan,
mannosan, and galactosan, respectively. This is an equivalent of 10–20 ng of the respective anhydrosugars in a sample, a value similar to that published in Kuo et al. (2008a).

3. Results and discussion

3.1. Levoglucosan in urban dust SRM 1649, 1649a, and 1649b

A recent paper by Kuo et al. (2008a) showed that the levoglucosan concentrations for SRM 1649a and RM 8785 (163.9 ± 11.8 and 158.4 ± 8.8 μg g⁻¹, respectively) are similar to values reported recently by Larsen et al. (2006) for a freezer-stored sample of SRM 1649a (162 ± 8 μg g⁻¹) and three filter replicates of RM 8785 (163 ± 37 μg g⁻¹). These results, presented in Fig. 1, suggest that levoglucosan can be reproducibly extracted from particulate phase materials under different laboratory conditions and so point to the potential comparative nature of such results. Moreover, the similar levoglucosan concentration observed for these two reference materials, under different experimental protocols and instrumentation, shows that levoglucosan is homogeneously distributed in this urban dust sample and is associated with ultrafine particulates (mean diameter from volume distribution in SRM 1649a is 34.6 ± 0.4 μm whereas the RM 8785 consists entirely of the fine fraction <2.5 μm). The comparative nature of these inter-laboratory data points to the potential for this urban dust to serve as a control material for levoglucosan analysis. However, in their manuscript, Kuo et al. (2008a) noted a discrepancy in the study by Larsen et al. (2006), which reported an anomalously low value for one sample of SRM 1649a stored at room temperature for 25 years (81.1 ± 9.4 μg g⁻¹). To explain this discrepancy, Larsen et al. (2006) hypothesized that levoglucosan may be unstable in solid samples over long periods. Since levoglucosan has been shown to resist both photochemical oxidation and acid catalyzed hydrolysis in atmospheric aerosols (Locke, 1988; Fraser and Lakshmanan, 2000; Simonet et al., 2004a), as well as diagenesis during long-term preservation in sedimentary deposits spanning several decades to 1000s of years (Elias et al., 2001; Hunsinger et al., 2008), we believe that the twofold difference between the cluster of SRM replicates and the anomalous value may instead be due to the compromised nature of this specific SRM or to an analytical artifact (in extraction methodology or quantitation).

To address this issue, we tested both an older version of the urban dust sample (SRM 1649) and two more recent versions of the SRM (1649a and 1649b) using two different surrogates (sedoheptulosan vs. d7-levoglucosan) and two different extraction protocols (DCM:MeOH vs. EA). Over time, the original urban dust standard has thus been separated into three size fractions with RM 8785 representing the ultrafine fraction (PM_{2.5}), SRM 1649b representing the size distribution <63 μm, and SRM 1649–1649a corresponding to the bulk material (<125 μm). First, under a DCM:MeOH solvent protocol, the replicate analyses of SRM 1649, 1649a, 1649b showed similar values in levoglucosan concentrations whether sedoheptulosan or d7-levoglucosan was used as a surrogate (Fig. 2). This demonstrates that a) sedoheptulosan can act as an appropriate (and less expensive) surrogate for the anhydrosugar analysis in environmental samples (cf. Simpson et al., 2004), and b) levoglucosan concentrations are unaffected by long-term preservation (~12 years) even under shelf (and dry) storage conditions. In all these experiments, the surrogate recovery, determined using 1,3,5 trisopropylbenzene, averaged 97 ± 7% for sedoheptulosan and 103 ± 7% for d7-levoglucosan. All these results plot within the range reported previously by Kuo et al. (2008a) and Larsen et al. (2006) for SRM 1649a and RM 8785 (Figs. 1 and 2) pointing to the comparative nature of these different size fractions.

3.2. Extraction efficiency and solvent choice

The use of EA during the extraction protocol produced very different levoglucosan concentrations with values being higher than the DCM:MeOH averages by ~80% when sedoheptulosan was used as the surrogate, or lower by ~30% when d7-levoglucosan was used as the surrogate (Table 1). In both cases, surrogate recovery was relatively low (~45% and ~80% for sedoheptulosan and d7-levoglucosan, respectively). The overall average using the d7-levoglucosan surrogate (111.5 ± 3.0 μg g⁻¹) is comparable to the low values obtained by Larsen et al. (2006) for their unfrozen sample (81.1 ± 9.4 μg g⁻¹).

These results thus raise a question as to the efficiency of extraction using solvent mixtures that do not include at least a small proportion of methanol. Indeed, repeated extractions of SRM 1649a with DCM:acetone (8:2, v/v) did not significantly increase the levoglucosan concentration (86 ± 15 μg g⁻¹; Larsen et al., 2006), suggesting that some other solvent combination is required to fully extract levoglucosan from all particle pores. In a recent paper, Jonker and Koelmans (2002) demonstrated that the extraction of PAHs from soot (which is relatively enriched in the

![Fig. 1. Comparison of levoglucosan concentrations measured in bulk urban dust (NIST SRM 1649a) and its ultrafine particulates (RM 8785). Values from white bars are from Kuo et al. (2008a), whereas those from dark bars are from Larsen et al. (2006). Error bars correspond to ±1 SD.](image1)

![Fig. 2. Levoglucosan concentrations measured in prior and recent versions of bulk urban dust (NIST SRM 1649 and 1649a, respectively) as well as the newer version of the urban dust sieved on a 63 μm sieve (SRM 1649b), using different surrogate standards. Dashed line corresponds to the published average value for SRM 1649a (Kuo et al., 2008a), whereas dotted lines represent the ±1 SD envelope around the average. Error bars correspond to ±1 SD.](image2)
SRM 1649a) could be explained by a two-step mechanism involving swelling of the sorbent matrix and subsequent displacement of sorbates by solvent molecules. The degree of swelling appeared however to be a function of the molar volume of the solvents, with small solvent molecules (e.g. methanol) causing significantly more swelling than larger ones and allowing for a more efficient solvent replacement of the sorbates (Jonker and Koelmans, 2002). Because of a lack of polar interactions between hydrophobic organic molecules and polar solvents, this swelling process is probably the main driving process for the observed enhanced extraction efficiency of HOCs by solvent mixtures containing small fractions of methanol. Alternatively, high extraction efficiencies of polar molecules and polar solvents, this swelling process is probably the main driving force of the lack of polar interactions between hydrophobic organic molecules and polar solvents. Because sedoheptulose contains an additional hydroxyl group compared to other sugars, its full extraction and retention in the solvent mixture is impossible (Fabbri et al., 2008b). For example, Simpson et al. (2004) showed that recovery of sedoheptulose from spiked quartz filters was unacceptable low when EA was used as a solvent. Because sedoheptulose contains an additional hydroxyl group compared to other anhydro sugars, it is not particularly soluble in EA and thus less efficiently extracted when polar interactions are possible with the matrix (Simpson et al., 2004). This point was highlighted in a recent study (Fabbri et al., 2008b), which showed that due to strong interactions between sedoheptulose and active sites on the GFF filters, the recovery of this surrogate was unacceptable low despite the use of methanol as an extracting solvent.

In the present study, despite the observed higher recovery for 4-deoxyglucosan, it is apparent that EA cannot extract all anhydrosugars from atmospheric particulates as efficiently as solvent mixtures containing some fraction of methanol (Table 1). The higher value obtained by Larsen et al. (2006) from a low temperature frozen sample (162 ± 8 µg g⁻¹) raised the possibility that the lower temperature freezing (−80 °C) could provide some particle pore disruption and thus increase extraction efficiency even in the absence of a polar solvent. In order to try to replicate the results from Larsen et al. (2006), we thus froze (−80 °C) sub samples of SRM 1649 and SRM 1649a for almost three months prior to extraction with EA. As shown in Fig. 3, this treatment did nothing to improve the extraction efficiency and further demonstrated the replicability of the prior results. Furthermore, although a potential particle swelling effect can still not be overruled, these lower recoveries point to a constant effect such as saturation of the apolar solvent. Hence, despite the lack of a demonstrated mechanism for higher extraction yields and surrogate recoveries in the DCM:MeOH extraction series, the present data do suggest that including some proportion of methanol improves the overall recovery and should thus be included in the extraction protocol.

Although we did not perform a systematic study to test a series of solvent ratios to extract levoglucosan (and isomers) from aerosol SRMs, in the course of our method development and further applications, we tested different solvent extraction approaches in addition to the experiments we present here. During an initial stage of testing, we used 100% MeOH (2 × 15 mL) using sonication as suggested by several studies (Fine et al., 2004; Simpson et al., 2004; Lee et al., 2008). The average levoglucosan concentration obtained from replicate extractions (n = 4) of SRM 1649a was 172.3 ± 6.3 µg g⁻¹, which is not statistically different than the values presented in Table 1. Subsequently, we tested a different DCM:MeOH ratio (2:1, v/v) under accelerated solvent extraction and included an internal standard to calculate surrogate recoveries. The results of replicate analyses of SRM 1649a (n = 7; 162.3 ± 6.3 µg g⁻¹, surrogate recovery of 102 ± 10%) were again not statistically different than the values presented in Table 1. Although a smaller proportion of MeOH (DCM:MeOH > 9:1) could potentially be used to quantitatively extract levoglucosan from filters, the incorporation of a measurable amount of MeOH is important to permit particle swelling and a more efficient extractions of components sorbed into inner pores of aerosol particles (Jonker and Koelmans, 2002).

3.3. Anhydrosugar concentrations in a series of urban dust SRMs

In addition to levoglucosan, we also quantified the concentrations of two of its isomers (mannosan and galactosan) in the SRMs. In the Washington, D.C. urban dust SRM series, no significant difference was observed in the concentrations of the three anhydrosugars for all size fractions (Table 2) pointing to the homogeneous distribution of biomass-combustion by-products across the size continuum of this aerosol. The present results are consistent with similar conclusions from two earlier studies (Larsen et al., 2006; Kuo et al., 2008a), which reported statistically identical

Table 1

| Concentrations, µg g⁻¹ (±1SD) of levoglucosan in SRM 1649a and 1649 using two extraction protocols (DCM:MeOH, 9:1, v/v; EA, 100%) as well as two surrogate standards (sedoheptulosan and 4-deoxyglucosan). |
|---|---|---|---|---|
| Sedoheptulosan | d₄-Levoglucosan | DCM:MeOH | EA |
| Recovery (%) | Recovery (%) | Recovery (%) | Recovery (%) |
| SRM 1649a | 160.6 ± 4.7 | 112.0 ± 4.3 | 98 ± 5% | 47 ± 2% |
| SRM 1649 | 160.2 ± 4.8 | 111.0 ± 1.9 | 98 ± 5% | 43 ± 1% |

Table 2

| Concentrations, µg g⁻¹ (±1SD) and ratios of anhydrosugars in Washington, D.C.’s urban dust (SRM 1649, 1649a, and 1649b) as well as Prague’s urban Dust (SRM candidates 2786 and 2787). Data produced using d₄-levoglucosan as surrogate standard. |
|---|---|---|---|
| Size fraction | Bulk | Bulk | Bulk |
| µM | µM | µM |
| Levoglucosan | 163.9 ± 7.0 | 160.5 ± 4.7 | 160.5 ± 5.0 | 464.7 ± 8.8 | 495.8 ± 5.4 |
| Mannonosan | 17.5 ± 0.9 | 17.3 ± 1.0 | 16.7 ± 0.7 | 94.7 ± 1.9 | 1005 ± 1.6 |
| Galactosan | 5.2 ± 0.3 | 5.0 ± 0.3 | 4.8 ± 0.2 | 33.2 ± 1.0 | 35.3 ± 0.8 |
| L/M | 9.4 ± 0.5 | 9.3 ± 0.4 | 9.6 ± 0.3 | 49 ± 0.0 | 49.0 ± 0.0 |
| L/(M + G) | 7.2 ± 0.3 | 7.2 ± 0.3 | 7.5 ± 0.1 | 36 ± 0.0 | 37 ± 0.0 |
Levoglucosan values between the ultrafine fraction and the bulk material of this urban dust SRM (see Fig. 1). The candidate SRMs from the Czech Republic (2786 and 2787) are characterized by 3- to 7-fold higher anhydrosugar concentrations than those observed in the Washington, D.C. urban dust (Table 2). Although the ultrafine fraction (<4 μm) shows statistically significant lower concentrations than those from the fine fraction (<10 μm), the difference is only ~6%, again suggesting a relative homogeneity in the distribution of biomass-derived combustion by-products in these atmospheric particles. In addition, since levoglucosan production is highly dependent on combustion temperature (Kuo et al., 2008a), these findings also confirm that low temperature biomass combustion contributes substantially to the very fine fractions of atmospheric PM.

The relative homogeneity of levoglucosan distribution observed in the two aerosol SRMs appear at odds with a series of experiments performed recently during a prescribed burning event in Taiwan (Lee et al., 2008; Engling et al., 2009). Both studies reported a bimodal distribution of levoglucosan in aerosols with approximately 50:50% distribution in the ultrafine and large PM (PM2.5). This bimodal distribution, however, becomes much less important in a suburban site removed from the emission source with less than 30% of levoglucosan remaining larger than 10 μm during the prescribed burning event, decreasing to less than 5% during harvest-background season (Lee et al., 2008). These studies further suggest that the particle-distribution of levoglucosan in aerosols produced from the burning of rice straw may be specific to the particular burning practices of this agricultural residue combined with related combustion and regional environmental conditions (soil water content, relative humidity, fire conditions). The relative predominance of PM2.5 levoglucosan distribution at the suburban site also suggests that large PM settled out of the atmosphere rapidly through dry deposition (Lee et al., 2008; Engling et al., 2009).

There thus seem to be no contradiction between the present results on size fractions and those from the Taiwanese rice burning studies. The two SRMs used in the present study are both urban and thus far removed from potential agricultural burning practices and eventual wildfires, which should have limited the incorporation of combustion-derived large PM in sampled aerosols. In addition, both SRMs integrate an entire year of deposition, which would have averaged potential differences observed during instantaneous combustion events such as those reported during agricultural burning events (Lee et al., 2008; Engling et al., 2009). This may lead us to reassess the conceptual definition of combustion-derived carbonaceous particles, which presently characterizes low temperature charred biomass materials as generally comprised of large particles with short atmospheric residence time (Masiello, 2004). The important presence of this biomarker in ultrafine particles suggests that our conventional view of size distribution decreasing and atmospheric residence time increasing along the char to soot continuum may have to be revised to include these small char particles (Kuo et al., 2008a), which are themselves characterized by long atmospheric residence times and transport ranges.

Finally, we compared the relative proportions (ratios) of levoglucosan to mannosan and galactosan in the two SRM series since the proportional yields of these various anhydrosugars provide valuable information for source reconstruction of combustion-derived by-products in atmospheric aerosols (Fabbri et al., 2008a, 2009; Schmidl et al., 2008; Caseiro et al., 2009). For example, the combustion of low-rank brown coals containing fossilized cellulose (i.e. xylitic lignite) can generate large amounts of cellulose-derived levoglucosan but only negligible amounts of hemicellulose-derived mannosan and galactosan (Fabbri et al., 2008a, 2009). Hence, a levoglucosan to mannosan ratio (L/M) greater than 50 in atmospheric particles may be used to infer predominant combustion inputs from very specific poor-quality brown coals (Fabbri et al., 2009). Additionally, the ratio of levoglucosan to mannosan (and galactosan) also varies depending on the type of biomass combusted (Caseiro et al., 2009; Fabbri et al., 2009). For example, differences in the L/M ratio in smoke from softwood and hardwood/grass combustion (~5 vs. ~10–20, respectively) can further help discriminate between inputs from these combustion sources to the atmosphere (Ward et al., 2006; Schmidl et al., 2008; Caseiro et al., 2009; Fabbri et al., 2009). In addition, a recent study by Engling et al. (2009) shows that herbaceous tissues can generate relatively high levoglucosan/mannosan ratios (L/M: 25–50). This adds new insights into the signature of biomass smoke showing that the combustion of herbaceous tissues can generate L/M signatures that are much higher than those from woods of deciduous trees (10–20) and closer to low-rank brown coals (~50). Although more work is needed to better constrain the source signatures of biomass combustion, it seems that softwoods and hardwoods are characterized by relatively low L/M ratios, whereas brown coals and herbaceous tissues generate much higher L/M ratios.

In all the NIST SRMs studied, the low L/M ratios (<10) suggest that wood combustion inputs, rather than herbaceous biomass or brown coal, are the predominant source of anhydrosugars in the atmospheric PM, at least at the time of the sampling. In addition, these ratios point to a mixture of hardwood/softwood input to the Washington, D.C. SRM (L/M = 9.4) but a predominantly softwood source in the Czech SRM (L/M = 4.9). The signature of combination of hardwoods and softwoods combustions in the Washington, D.C. SRM is consistent with high concentrations of hardwood- and softwood-derived lignin in this aerosol (Louchouarn et al., in review). The compositional differences in lignin structure between hardwoods (angiosperms) and softwood (gymnosperms) provide a means for discriminating between diverse taxonomic vascular plant groups in complex environmental mixtures (Góñi et al., 1998; Louchouarn et al., 1999, in review; Hedges et al., 2000; Kuo et al., 2008b). For example, because syringyl structural units are only incorporated in significant amounts into angiosperm lignin but are virtually absent from gymnosperm tissue (Sarkanen and Ludwig, 1971), a ratio of syringyl (S) to vanillyl (V) phenols appreciably greater than zero is indicative of the presence of at least some angiosperm tissue (Hedges and Mann, 1979; Góñi and Hedges, 1992; Louchouarn et al., 1999; Kuo et al., 2008b). The difference in syringic acid to vanillic acid ratios (Sd/Vd), two predominant methoxyphenols derived from biomass combustion (Simonet, 2002; Kuo et al., 2008b), in the solvent extracts of both SRMs further confirms a higher proportion of angiosperm in the Washington, D.C. aerosol versus the Prague aerosol. (0.41 ± 0.05 vs. 0.11 ± 0.01, respectively. Data not shown.) Although the predominance of softwood combustion in the Czech SRM is itself consistent with similarly low L/M signatures and softwood sources in combustion-derived aerosols of central Europe (Caseiro et al., 2009), the absence of evidence for brown coal inputs in this sample is particularly striking. Brown coal combustion has been recognized to contribute up to 1/3 of all fuel used in thermoelectric plants of this region of Central Europe (Bridgman et al., 2002; Brans and Domasova, 2003; Fabbri et al., 2008a). In fact, the border zone area between southeast Germany, Southwest Poland, and Northwest Czech Republic is known colloquially as the “Black Triangle” for its history of atmospheric pollution derived from brown coal combustion from industrial activities and thermoelectric power generation (Bridgman et al., 2002). One would thus expect to see at least some levoglucosan emissions derived from such industrial combustion activities, yielding characteristically high L/M ratios (Fabbri et al., 2008a, 2009). However, because of the strong dependence of levoglucosan production on combustion temperature, industrial/thermoelectric boilers may not contribute substantial inputs of levoglucosan to
atmospheric PM. In contrast, the less efficient combustion of brown coal in domestic boilers may act as a more significant source of levoglucosan emissions. For example, as recently as the late 1990s brown coal combustion has been estimated to be greater than biofuel (wood, briquets) usage by a factor of 2.5–3.0 on a weight per weight basis in a Czech village a few kilometers away from Prague (Branis and Domasova, 2003). However, because levoglucosan emissions from brown coals have been exclusively linked to low-rank xylite lignites, the lack of coal signature in the anhydrosugar composition of the Prague aerosols does not preclude the possibility that other brown coals are still important fuel sources both locally and regionally. In the Prague aerosols, however, the very high anhydrosugar concentrations, and characteristically low L/M ratios and Sd/Vd ratios, all suggest that softwood combustion was the predominant source of biomass-derived combustion particles in the region at the time of sampling.

4. Conclusions

With increasing attention devoted to the source apportionment of atmospheric PM, and in particular to the characterization of biomass-derived combustion aerosols, comprehensive method validation for biomarker quantification needs to be standardized. One approach is to evaluate analyte recovery and extraction efficiencies based on certified concentrations in a series of standard reference materials (SRMs). NIST and other National Meteorology Institutes produce such certified reference materials and provide updates to include emerging analytes of interest on their Certificate of Analysis. Levoglucosan (and its isomers) will be incorporated into the certificates of aerosols (Schantz et al., 2005). However, despite the widespread use of this organic biomarker to reconstruct biomass combustion inputs to the atmosphere as well as soils and sediments (Simoneit et al., 1999; Fine et al., 2004; Simpson et al., 2004; Jordan et al., 2006; Larsen et al., 2006; Kuo et al., 2008a; Caseiro et al., 2009; Fabbri et al., 2009), a comprehensive method validation is still lacking. Extraction protocols, solvent choices, and quantification methods are diverse. The widespread availability of SRMs would strengthen method validation and intercomparison of data across fields, study sites, and research groups. As with any other analytical technique, anhydrosugar quantification would benefit from having a series of readily available standards that could be used to insure inter-laboratory consistency of the data produced. To our knowledge, the study from Larsen et al. (2006) is the only one to document levoglucosan concentrations in NIST SRMs. Recent analyses of some of these materials (Kuo et al., 2008a) showed promise in the comparative nature of some of these results, yet also raised concerns with respect to some inconsistencies in the reported data. The present study has thus tested the extraction efficiency and quantification reproducibility of anhydrosugars in a series of NIST SRMs using two extraction protocols and isotopically-labeled (d7-levoglucosan) vs. chemically analogous (sedoheptulose) surrogates. In both instances, levoglucosan concentrations in the different versions of the Washington, D.C. urban dust standard (SRM 1649, 1649a, 1649b, and RM 8785) were similar. The present test also showed that levoglucosan concentrations were not affected by long-term shelf storage of dry material. Variability of analyses were similar for both surrogates and averaged <5%. Surrogate recoveries were shown to average 103 ± 7% and 97 ± 7% for d7-levoglucosan and sedoheptulose, respectively. The choice of solvent was shown to affect recoveries the most (but not variability). Levoglucosan concentrations were either underestimated or overestimated with ethyl acetate extraction when d7-levoglucosan or sedoheptulose was used as surrogate, respectively. These results point to the need to use some fraction of polar solvent (i.e. methanol) in the solvent mixture. Anhydrosugar concentrations in the urban dust from the Czech Republic (candidate SRMs 2786 and 2787) were characterized by 3- to 7-fold higher anhydrosugar concentrations than those observed in the Washington, D.C. urban dust. The internal anhydrosugar signatures (i.e. L/M ratio) confirm the predominance of biomass combustion sources in both SRM series with mixed inputs from hardwood and softwood combustion in the Washington, D.C. urban dust and a predominantly softwood source in the Prague urban dust. The uniform distribution of anhydrosugars across the particle size distribution of both SRM series confirms earlier studies that low temperature charred materials contribute significant inputs to atmospheric ultrafine particles with long atmospheric residence time and transport ranges.

Although the wide range of concentrations reported in these two SRM series provide an interesting working range of standards from which to start an intercomparison, the SRMs presented here are in no way exhaustive indicators of all the potential source and site indicators that can be used for atmospheric PM source reconstructions. Additional certified standards should be identified to include materials with both very low (pristine) as well as high concentrations (biomass and brown coal impacted sites). As the international research community works towards the identification and certification of a series of reference materials though an inter-laboratory ‘round-robin’ approach (Hammes et al., 2007), we thus suggest that the presented SRMs could be used initially as working standards for assessing the analytical consistency of levoglucosan and its isomers.

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