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Validation of a HILIC/ESI-MS/MS method for the wood burning marker levoglucosan and its isomers in airborne particulate matter

F. Mashayekhy Rad [a], S. Spinicci [a], S. Silvergren [b], U. Nilsson [a], R. Westerholm [a,*]

[a] *Department of Environmental Science and Analytical Chemistry, Stockholm University, SE-106 91, Stockholm, Sweden*
[b] *Environment and Health Administration, SLB-analys, Box 8136, SE-104 20, Stockholm, Sweden*

HIGHLIGHTS

- Analysis of PM10 for the wood burning marker levoglucosan and its isomers.
- The analytical method requires no extensive sample preparation.
- The analytical method is fast.
- The analytical method was validated using SRM materials.
- The analytical method was applied on real samples.

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ABSTRACT

In the present study, a methodology involving hydrophilic interaction liquid chromatography (HILIC) and electrospray (ESI) tandem mass spectrometry (MS/MS) was developed for measurement of anhydrous monosaccharides as markers for wood burning in atmospheric aerosols, PM_{10}. No extensive sample preparation, other than ultrasound-assisted solvent extraction and evaporation, was applied. A penta-hydroxysilica column enabled separation of levoglucosan from mannosan and galactosan within 5 min and the quantitative performance was validated using the standard reference materials (SRM) 1649a and 1649b. The experimentally obtained results for SRMs were in agreement with values previously reported in other studies. Achieved instrumental limits of detection (LODs) were below 10 pg injected on column, corresponding to LODs in air lower than 0.10 ng/m^3 for all measured isomers for 2–3 day sampling with 1.0 m^{-3} h^{-1} sampling rate.

The validated method was used for the determination of levoglucosan and its isomers in atmospheric aerosols collected in three different Swedish urban areas during the winter and summer time in 2017. The total measured concentrations for levoglucosan and galactosan + mannosan were determined to be between 78 and 167 ng/m^3 in January 2017, which is approximately 10-times higher compared to the levels detected in July, reflecting the higher frequency of wood burning for heating during the cold season. Calculated concentration ratios between levoglucosan and its isomers in the urban area samples indicated mostly mixed softwood/hardwood combustion in winter time; on the other hand, softwood burning was observed as the major emission in summer time.

1. Introduction

Biomass combustion, known as a major worldwide source of air particulate matter (PM), has a direct impact on both human health and global climate (Bond et al., 2004). Combustion of wood generates particles containing a complex mixture of organic compounds (Hedberg et al., 2002; Avagyan and Westerholm, 2017; Nystrom et al., 2017). Several pollutants emitted are considered potentially harmful such as black carbon and polycyclic aromatic hydrocarbons (PAHs), especially benso(a)pyrene (BaP). Particulate matter may be emitted directly after incomplete combustion or formed in the atmosphere after emission due to condensation of volatile organic compounds or due to chemical transformations (Nussbaumer et al., 2008). Commercial, institutional and household

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* Corresponding author.
E-mail address: roger.westerholm@aces.su.se (R. Westerholm).

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emissions due to biomass and coal burning constitute the single largest source of $PM_{2.5}$ (particle sizes below 2.5 μm) within EU 2014 (EMEP/EEA, 2016). But the uncertainties in emission estimates are very large due to e g lack of information on amount of wood burnt in household stoves and boilers, type of wood and whether the wood is dry or wet. In addition, countries use different methodologies of measuring and estimating emissions from residential wood burning appliances.

In the year of 2000, it was estimated that the residential wood combustion in the Nordic countries contributed with 12–69% of the mass of airborne $PM_{2.5}$ (Karvosenoja et al., 2004).

Cellulose is one major component and its content varies between 40 and 50% of the weight of dry wood (Young, 1984a). Anhydrous monosaccharides have been shown to be formed from the pyrolysis of cellulose, under conditions when the combustion of wood is incomplete in presence of air (Simoneit, 2002). Among these monosaccharides, levoglucosan has been shown to be the major isomer released from wood burning, while mannosan and galactosan occur at lower levels (Young, 1984b; Simoneit, 1999; Schkolnik and Rudich, 2006). Levoglucosan has been found to be relatively stable in atmospheric aerosols (Fraser and Lakshmanan, 2000) and since it has not been detected in emissions from diesel combustion or in coal reference standard materials (SRM 2975 and SRM 1632c, respectively) (Kuo et al., 2008), it has been used as a tracer for wood combustion in ambient particulate material (Zappoli et al., 1999; Fraser and Lakshmanan, 2000; Simoneit, 2002; Hedberg et al., 2006), as in the apportionment of different emission sources (Hennigan et al., 2010). Furthermore, it has been suggested that the abundance ratio of levoglucosan and the sum of mannosan and galactosan in collected air samples reflects the type of biomass fuels combusted. As an example, a ratio between 4.5 and 14 (oak wood and cottonwood) is considered to indicate mainly hardwood combustion, while 2.4–5 (ponderosa pine) reflects more of softwood burning (calculated from Engling et al., 2006). Vicente and Alves (2018) recently critically reviewed particulate matter emission factors and evaluated the suitability of specific organic markers.

Analytical methods so far reported for airborne anhydrous monosaccharides include gas chromatography/mass spectrometry (GC/MS) after silylation of the highly polar compounds (Schkolnik and Rudich, 2006). Silylation is a labor-intensive procedure and another drawback is that the formed derivatives are unstable over time and the derivatized samples therefore have to be analyzed within 2 days (Wan and Yu, 2007). Derivatization methods for levoglucosan and monosaccharide anhydrides have been reviewed by Hsu and co-workers (Hsu et al., 2007). Also GC without derivatization has been reported in the literature (Fraser and Lakshmanan, 2000; Fine et al., 2002; Zdráhal et al., 2002), although resulting in relatively poor chromatography with unsymmetrical peak shapes. Furthermore, high-performance anion exchange chromatography (HPAEC) coupled to pulse amperometric detection (PAD) (Schkolnik and Rudich, 2006) or electrospray ionization-tandem mass spectrometry (HPAEC/ESI-MS/MS) (Asakawa et al., 2015; Saarnio et al., 2010) has been used. A shortcoming with HPAEC coupled to ESI is that it requires the use of a suppressor device to handle the high levels of salt involved, which makes the instrument setup more complex. Reversed-phase liquid chromatography (RPLC) coupled to ESI-MS/MS has also been employed (Dye and Yttri, 2005), as well as hydrophilic interaction liquid chromatography (HILIC)/ESI-MS/MS for the measurement of anhydrous monosaccharides in various matrices, such as Antarctic ice (Gambaro et al., 2008), soil, sediments (Hopmans et al., 2013) and snow (You et al., 2016). In addition, HILIC/ESI with high-resolving Fourier transform mass spectrometry has been used for separation and detection of the compounds in both aerosol and snow samples (Matějíček and Vašíčková, 2016).

In this study, isocratic HILIC was used in combination with ESI-MS/MS, in order to set up a fast analytical method for the determination of levoglucosan and the sum of mannosan and galactosan in PM_{10} particulate air, sampled in three suburban areas in Sweden. Aerosol samples were taken both wintertime and during summer months, respectively, in order to represent periods when high and low emissions from wood burning are expected. The analytical methodology was validated using the air particle Standard Reference Materials (SRM) 1649a and 1649b (urban dust).

2. Materials and methods

2.1. Chemicals

Levoglucosan (1, 6-anhydro-β-D-glucose), 99%, was purchased from Sigma-Aldrich (St. Louis, MO, USA). Both galactosan (1,6-anhydro-β-D-galactose) and mannosan (1,6-anhydro-β-D-mannose), both > 95%, were obtained from Cayman chemical (Ann Arbor, MI, USA). The surrogate internal standard (IS), levoglucosan-$^{13}C_6$, >98%, was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Acetonitrile of LC/MS grade was obtained from VWR (Radnor, PA, USA). Ultrapure water (resistivity $>18\ M\Omega\ cm^{-1}$) was obtained from a Milli-Q plus system from Millipore (Bedford, MO, USA).

Both SRM 1649a and 1649b, with nominal particle size ≤125 and ≤ 63 μm, respectively, were obtained from National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA).

2.2. Sampling location and conditions

Sampling was performed in parallel at three different sampling sites in Sweden, namely Ytterjärna (59°05′N 17°34′E) in Södertälje, Enskede (59°16′N 18°02′E) in Stockholm and Delsbo (61°48′N 16°33′E) in Hudiksvall, during both January and July in 2017. A sequential sampler SEQ47/50 (Sven Leckel, Berlin, Germany) equipped with a PM_{10} impactor inlet, designed for outdoor use at varying temperatures and environmental conditions, was employed for each collection of airborne particles. Micro-quartz fiber filter, grade T293 (Munktell, Helsinki, Finland) was used for sampling and the air sampling rate was $1.0\ m^3/h$. In January and July the sampling periods were 24 and 48 h, respectively. Blank samples were filters used during the same sampling period, but without pumping any air through the sampler, and then analyzed in the same way as the sample filters.

2.3. Standard solutions and sample preparation

Individual stock solutions of levoglucosan, mannosan, galactosan and ^{13}C-labelled levoglucosan (IS) were all prepared at a concentration of 100 μg/mL in water, where after working matrix-free standard solutions were made from them by series of dilutions using water/acetonitrile 5/95 (v/v). The final concentrations at six levels were within the range 0.01–15 μg/mL.

Each sampled filter was first spiked with 1 μg of IS and then ultrasonically extracted twice in 10 mL of ultrapure water for 10 min. After ultrasonication, the two extracts were transferred to a pear-shape flask (Pyrex® glass) and vacuum-dried by a rotary evaporator (RII, BUCHI, Flawil, Switzerland) at 40 °C. All used glassware had previously been washed twice with ultrapure water and then incubated for 1 h at 150 °C prior use. The obtained residue after evaporation was dissolved in 500 μL of water/acetonitrile (5/95 v/v). From this solution a 10-μL volume was injected into LC/MS system.