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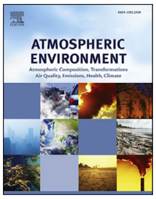

Technical note

Rapid and sensitive quantification of levoglucosan in aerosols by high-performance anion-exchange chromatography with positive electrospray ionization mass spectrometry (HPAEC-positive ESI-MS)

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ABSTRACT

A convenient quantification method for underivatized levoglucosan, which is a tracer for biomass burning influenced particulate matter (PM), has been established using high-performance anion-exchange chromatography (HPAEC) coupled to positive electrospray ionization mass spectrometry ((+)ESI-MS). Levoglucosan was chromatographically separated from its isomers (mannosan and galactosan) and detected selectively with positive ESI-MS. Limits of detection and quantification for this method were 0.40 and 1.3 ng mL^{-1}, respectively. A comparison of simultaneous measurements by this method and conventional derivatization gas chromatography/mass spectrometry showed a good linearity with a slope of 1.008 and a determination coefficient of 0.9932. The developed method was applied to ambient suspended particulate matter hourly collected by continuous particulate monitors at 10 stations. The hourly concentration of levoglucosan during August 9–11, 2011, was 1.7–918 ng m^{-3} and its distribution indicated the transportation of biomass burning aerosols of a forest fire. This is the first report of horizontal distribution of the hourly levoglucosan concentration in Japan.

1. Introduction

Biomass burning is an important source of atmospheric particulate matter (Crutzen and Andreae, 1990) and the biomass burning aerosols affect the climate (Schkolnik and Rudich, 2006) and human health (Laumbach and Kipen, 2012). Forest fire (Saarnio et al., 2013) and domestic wood burning (Saffari et al., 2013) result in an increase in the concentration of the biomass burning aerosols in urban atmosphere. Moreover, it is suggested that aerosols originated from combustion of agricultural residues contribute to concentration of fine particulate matters in urban atmosphere in Japan (Kumagai et al., 2010).

To estimate the contribution of biomass burning aerosols to atmospheric particulate matter concentrations, several studies have been performed to quantify a molecular marker levoglucosan (1,6-anhydro-β-D-glucopyranose). The levoglucosan has been primarily measured by gas chromatography/mass spectrometry (GC/MS) after trimethylsilylation (e.g. Simoneit et al., 1999). This method, however, requires organic solvent extraction, concentration, and derivatization steps, making levoglucosan analysis time- and cost-consuming. Therefore, several methods for detection of underivatized levoglucosan were developed using liquid chromatography with pulsed amperometric detection (PAD) or mass spectrometry (MS) (Schkolnik and Rudich, 2006). Because MS can detect target analytes more selectively than PAD (Guignard et al., 2005), complete chromatographic separation of analytes and contaminants is not necessary for MS analysis. This advantage of MS is beneficial for rapid analysis, which has difficulty in separating analytes within short analytical time. Moreover, errors in extraction procedure and injection volume are negligible when stable isotope-labeled levoglucosan is used as an internal standard for MS analysis (Stokvis et al., 2005). Although MS detector is more expensive than PAD, MS detector for liquid chromatography is becoming popular.

Recently, combination with high-performance anion-exchange chromatography (HPAEC) and MS detection was proposed by Saarnio et al. (2010) for determination of levoglucosan in aerosols. They used potassium hydroxide solution as an eluent and ionized levoglucosan using the electrospray ionization (ESI) technique in

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negative-ion mode. Piot et al. (2012) also quantified levoglucosan and its isomers in negative-ion ESI in diluted sodium hydroxide (NaOH) eluent. It should be noted that alkali metal ions, such as Na$^+$, produces positively adduct ions of levoglucosan (Gao, 2003). Wan and Yu (2006) indicated that the sodiated molecues ([M + Na]$^+$) and ammonium ion adducts ([M + NH$_4$]$^+$) were dominant in ESI mass spectra of levoglucosan in sodium chloride and ammonium acetate solutions, respectively. They also suggested the enhancement of sensitivity of the positively adduct ion by addition of methanol. Therefore, ESI in the positive-ion mode may be suitable for detection of levoglucosan in NaOH solution, which is commonly used as HPAEC eluate.

Here, we describe a HPAEC-positive ESI-MS method for sensitive determination of levoglucosan. To prevent deposition of sodium salt around the interface of the MS, an excess of sodium ion was removed by a membrane suppressor. This method allows separation of levoglucosan from its isomers and rapid analysis of multiple samples. We validated this method and compared with derivatization GC–MS method. Our method was applied for measuring levoglucosan in suspended particulate matter (SPM) collected on filter tapes of continuous particulate monitors. This is the first study to show the hourly levoglucosan concentrations in the atmosphere in Japan.

2. Materials and method

2.1. Sample collection

To evaluate compatibility with derivatization GC–MS method, fine atmospheric particles (particles with a 50% cut-off aerodynamic diameter of 2.5 μm, i.e., PM$_{2.5}$) were collected onto precombusted (800 °C, 3 h) quartz fiber filters with 47 mm diameter (2500QAT-UP, Pallflex products Corp., Putnam, CT, USA). PM$_{2.5}$ samples were collected with Partisol®-Plus model 2025 sequential air sampler (Thermo Fisher Scientific Inc., Franklin, MA, USA) at a flow rate of 16.7 L min^{-1} for 6 or 24 h in Osaka, Japan, in February 2013. The quartz filters were cut into half for further analysis.

SPM (particles with a 100% cut-off aerodynamic diameter of 10 μm) samples were automatically sampled hourly by continuous particulate monitors at 10 air monitoring stations. The location of the stations is shown in Fig. 1. The particulate monitors used were SPM613/model-333 β (Kimoto Electric Co., Ltd., Osaka, Japan), APDA361 (HORIBA Ltd., Kyoto, Japan), and DUB357/GRH-106 (DKK-TOA Co., Tokyo, Japan). These monitors collected SPM on glass fiber filter tapes at a flow rate of 16.7 or 18.0 L min^{-1}. The filter tape samples were stored at −20 °C until analysis. Each SPM spot, which was collected during August 9–11, 2011 (Japan standard time), was punched out (11 mm in diameter) for extraction. A large forest fire occurred about 50 km away from the monitoring station "A" in the southeast direction in August 9, 2011.

2.2. HPAEC-positive ESI-MS analysis

For the 47 mm quartz filters, one-half of each filter was extracted in 10 mL of deionized water after addition of 1000 ng of internal standard (^{13}C$_6$-levoglucosan, Omicron Biochemicals Inc., South Bend, IN, USA). For the filter tape samples, each spot containing the internal standard (50 ng) was extracted in 0.5 mL of deionized water in a filter vial (Mini Uni-prep, Whatman, NJ, USA). These suspensions were sonicated for 30 min and were filtered using a 0.45 μm filter (polypropylene or hydrophilic PTFE).

The HPAEC-positive ESI-MS analysis was carried out using a Waters Alliance 2695 separation module (Waters, Milford, MA, USA) coupled with Waters Xevo® TQ MS. Sample aliquots (10 μL) were injected onto a Carbopac® PA-1 guard (10 μm, 2 × 50 mm; Dionex, Sunnyvale, CA, USA) and analytical columns (10 μm, 2 × 250 mm). The column was maintained at 30 °C. The elution was performed with a gradient of NaOH solution at a flow rate of 0.25 mL min^{-1}. The gradient condition of the NaOH concentration was as follows: 0–2 min, 2 mM; 2–7 min, 2–10 mM; 7–10 min, 10–200 mM; 10–11 min, 200 mM; 10–10.1 min, 200–2 mM; 10.1–15 min, 2 mM. Excess sodium ions in column eluate were removed by a suppressor (ASRS® 300, 2-mm; Dionex) in external mode. Before ionization, methanol was added into the eluate by a T-connector at a flow rate of 0.075 mL min^{-1}. Detection was achieved in the positive-ion ESI under the following conditions: capillary voltage, 2.8 kV; cone voltage, 18 V; source temperature, 150 °C; desolvation temperature, 400 °C; desolvation gas flow, 800 L h^{-1}; cone gas flow, 10 L h^{-1}. [M + Na]$^+$ of levoglucosan and the internal standard were respectively monitored with *m/z* 185.1 and *m/z* 191.1 by selected ion monitoring mode. Authentic standards of levoglucosan (Sigma–Aldrich, St. Luis, MO, USA), mannnosan (1,6-anhydro-β-D-mannopyranose; Toronto Research Chemicals Inc., Toronto, Canada), and galactosan (1,6-anhydro-β-D-galactopyranose; Molekula, Dorset, UK) were used for identification and quantification. Quantification was achieved using the internal standard calibration method.

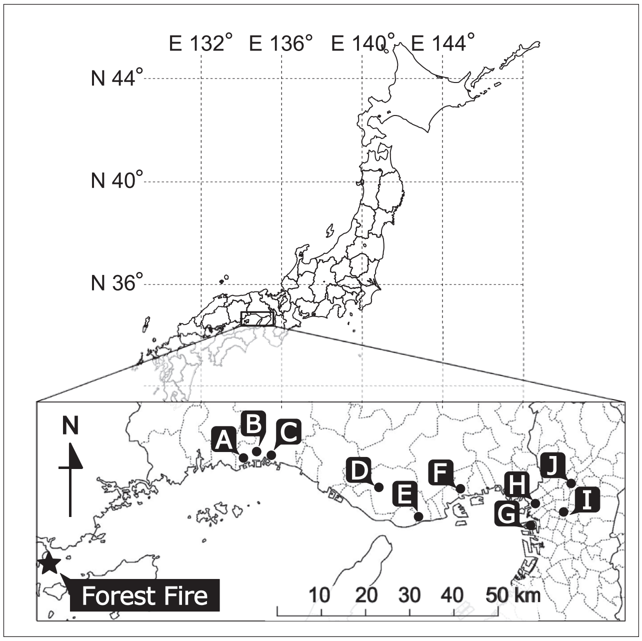

Fig. 1. Locations of suspended particulate matter (SPM) sampling stations.

2.3. Derivatization GC–MS analysis

The PM$_{2.5}$ samples were analyzed simultaneously by derivatization GC–MS as described in Kumagai et al. (2010). In brief, one-half of each filter was extracted with a dichloromethane and methanol mixture (2:1, *v*/*v*) and dried by a nitrogen stream. Silylation was performed using 50 μL of *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide containing 1% of trimethylchlorosilane (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and 200 μL of dichloromethane and hexane mixture (1:1, *v*/*v*) at 70 °C for 2.5 h. The derivatives were analyzed with a GC–MS (HP6890GC-HP5973MSD; Agilent Technologies, Inc. CA, USA) equipped with a capillary column (DB-5 MS, 30 m × I.D. 0.32 mm × 0.32 μm film thickness; Agilent Technologies, Inc.). Levoglucosan and internal standard were monitored with *m/z* 217 and *m/z* 220, respectively.