Note

A novel method for the rapid analysis of levoglucosan in soils and sediments

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ABSTRACT

We have developed a novel method, based on high performance liquid chromatography–mass spectrometry, for the rapid and quantitative analysis of levoglucosan in geological samples. Compared with existing methods, it does not require derivatization or extensive work up, and requires less sample material. Its validity is demonstrated by way of application to soil samples collected from a burned dune area and a late Quaternary marine sediment.

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1. Introduction

Biomass burning has a large impact on vegetation on land and is also a source of aerosol particles, which can have a significant impact on global climate (e.g. Crutzen and Andreae, 1990). Biomass burning seems to have increased in industrial times due to human activity (Simoneit, 2002 and references therein). However, in the geological past there have also been biomass burning events, as evidenced by e.g. elemental carbon records (Bird and Cali, 1998).

There are several tracers available for reconstructing past biomass burning events from ancient sediments and soils, including microscopic examination of charcoal or soot particles and the analysis of specific compounds such as polycyclic aromatic hydrocarbons (e.g. Denis et al., 2012). An important compound generated during burning of wood (Simoneit, 2002 and references therein) is levoglucosan (LVG, i.e.1,6-anhydro-β-D-glucopyranose). It is specific for biomass burning, as it is only generated via combustion of woody material, which contain sugars such as cellulose (e.g. Elias et al., 2001).

The most common technique for quantitatively analyzing LVG, particularly in geological materials, is gas chromatography–mass spectrometry (GC–MS) after derivatization with e.g. trimethylsilyl groups (Schkolnik and Rudich, 2006 and references therein). However, this technique is relatively time consuming, as it requires fractionation of the extract and appropriate derivatization. In addition to GC–MS, some high performance liquid chromatography (HPLC) methods, combined with, amongst others, MS detection, have been developed. These methods do not require LVG derivatization (Schkolnik and Rudich, 2006 and references therein). In particular, Gambaro et al. (2008) developed an HPLC-electrospray ionization (ESI)-MS^2 method with high sensitivity [detection limit 0.3 pg on column (oc)]. However, the method has only been applied to melted water from ice cores, which contain relatively little matrix compared with typical geochemical samples, while the applied LC separation used showed virtually no retention of LVG and therefore no great resolving power.

Here, we have developed a novel HPLC-MS^2 method for the rapid and quantitative analysis of LVG in complex sedimentary matrices and demonstrate its applicability for the rapid analysis of soils and marine sediments.

2. Material and methods

Standards (LVG, mannosan and galactosan) were from Sigma–Aldrich (St. Louis, MO). In 2011, soil samples were collected from a coastal dune area (52°42.41′N; 4°40.20′E) near the town of Schoorl (The Netherlands), where a large vegetation fire occurred in 2009. Finally, a marine sediment was taken from core MD03-2607 (36°57.64′S; 137°24.39′E) from the Murray Canyons area, offshore southeast Australia at 250 cm below sea floor and dated at 20.4 ka (Gingele and De Deckker, 2005).

The soil samples and sediment were freeze-dried, homogenized and extracted with MeOH, using automated solvent extraction (ASE; Dionex 350) at 100 °C and 107 bar. In order to remove salts from the marine sediment extract, it was dissolved in MeCN and filtered over a small 1 cm Na$_2$SO$_4$ Pasteur pipette column. Tests on soil extracts showed that this small column did not result in significant loss of LVG, with an average recovery of 101 ± 8% (n = 3). To evaluate the efficacy of different extraction solvents, one of the dune soil samples was extracted (3 x) with MeOH or a mixture of dichloromethane (DCM):MeOH (9:1, v:v) using ASE conditions as described above. All extracts were dissolved in MeCN containing 0.01% Et$_3$N and filtered using a regenerated cellulose 0.45 μm filter (Alltech, Deerfield, IL).

The extracts were analyzed using an Agilent 1100 series LC instrument (Agilent, San Jose, CA) coupled to a Thermo TSQ Quantum ultra EM triple quadruple mass spectrometer with an Ion Max

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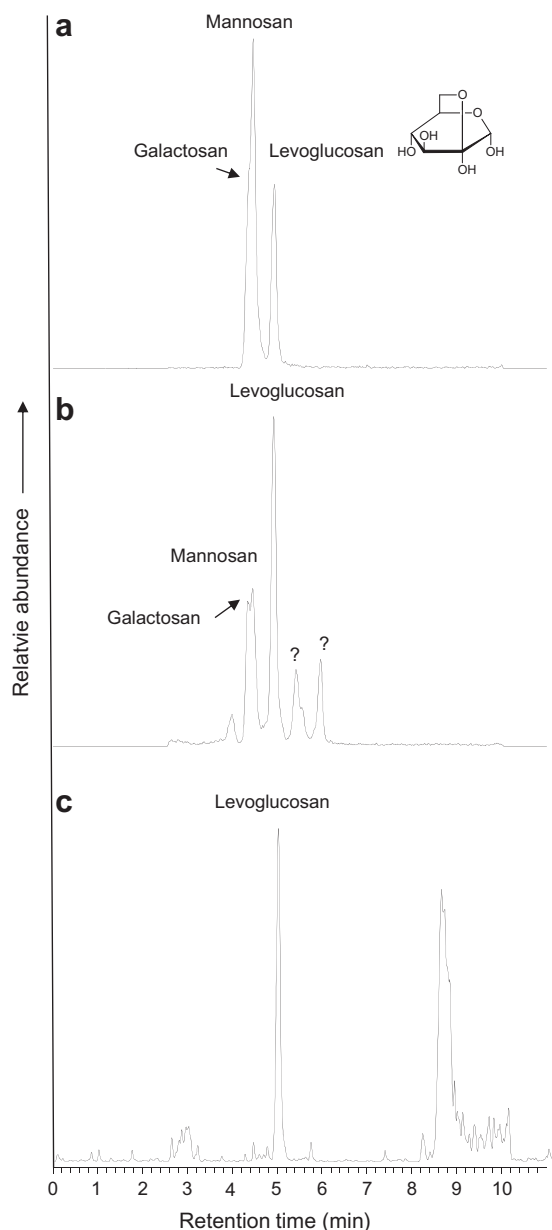
Fig. 1. HPLC-ESI-MS^2 total ion chromatogram of (a) standard mixture of LVG, mannosan and galactosan, (b) MeOH extract of a soil from a burned dune area (c) MeOH extract of a 20.4 kyr marine sediment from offshore southeast Australia. ESI spray was switched on between 2.5 and 10 min.

Source with ESI probe (Thermo Electron Corporation, Waltham, MA) operated in negative ion mode. Separation was achieved with a Luna NH$_2$ column (150 mm × 2 mm i.d.; 3 μm; Phenomenex, Torrance, CA) at 25 °C. Compounds were eluted (0.2 ml min^{-1}) with an isocratic mixture of 92.5% A:7.5% B (10 min) followed by back flushing with an isocratic mixture of 70% A:30% B (20 min) and re-equilibration at starting conditions (20 min). Eluent A was 0.01% Et$_3$N in MeCN and eluent B 0.01% Et$_3$N in water. Detection of LVG was achieved using selected reaction monitoring (SRM) and settings were optimized by direct infusion of a LVG standard solution. ESI settings were: capillary 300 °C, sheath gas (N$_2$) pressure 50 (arbitrary units), auxiliary gas (N$_2$) pressure 5 (arbitrary units) and spray voltage -4 kV. Ar (collision pressure 1 mTorr) was used as collision gas. SRM transitions monitored (collision energy in brackets) were m/z 161 (peak width Q1 = 0.2) to m/z 71

(15 V), m/z 85 (15 V), m/z 101 (12 V) and m/z 113 (11 V) (peak width Q3 = 0.7) with 0.1 s dwell time per transition.

LVG was quantified by integrating the peak area in the total ion chromatogram (addition of all transitions monitored) and comparison of the area with an external standard curve.

3. Results and discussion

We first optimized conditions for MS by infusion of a standard LVG solution with negative ion ESI, confirming the suitability of the SRM transitions described by Gambaro et al. (2008), i.e. m/z 161 to m/z 71, 85, 101 and 113. We then developed a new separation method, based on hydrophilic interaction chromatography (HILIC). Under these conditions a retention time of 4.9 min for LVG was obtained [vs. 1.5 min for Gambaro et al. (2008)], well away from the injection peak and thus potentially more suitable for analysis of LVG in geological samples with complex matrices. In addition, LVG was separated from its structural isomers mannosan and galactosan (Fig. 1a). This allows calculation of e.g. the ratio of LVG/(mannosan + galactosan), which can potentially be diagnostic for the type of burned biomass, i.e. hardwood vs. softwood and grass (e.g. Fabbri et al., 2009). Finally, the stability of the Luna NH$_2$ column up to pH 11 allowed direct modification of the mobile phase with Et$_3$N to pH 8–9, to enhance negative ion formation under the ESI conditions. The method does not therefore require post-column addition of NH$_4$OH as applied by Gambaro et al. (2008), making it relatively easier and more robust.

Sensitivity was tested via injection of varying amounts of LVG to give a linear response between 0.05 and 5 ng oc (r^2 0.99) and detection limit of ca. 25 pg oc. The method is therefore less sensitive than that reported by Gambaro et al. (2008), mainly due to the use of MeCN in the mobile phase instead of MeOH. Although MeOH improves LVG ionization, it substantially reduces retention on the column and is therefore not suitable for use with samples with a complex matrix. Still, the detection limit is comparable with the 21 pg oc reported using GC–MS by Louchouarn et al. (2009). However, they report a sample requirement of 10–20 ng LVG per sample, while for our LC-MS method it is 100–200 pg LVG per sample, thereby requiring much less sample material.

To evaluate suitable extraction solvents, we extracted a soil sample from a burned dune area, which was likely to contain a high level of LVG. We first tried extraction with MeOH, as it is commonly used for LVG extraction (e.g. Elias et al., 2001) and LVG was indeed readily detected at a concentration of 2.62 ± 0.13 (n = 3) μg g^{-1} soil (Fig. 1b). We also evaluated DCM:MeOH (9:1), as it is regularly used for ASE extraction of geochemical samples and DCM:MeOH has successfully been used for LVG extraction from air filters (Pashynska et al., 2002). A statistically indistinguishable concentration of 2.61 ± 0.28 μg g^{-1} soil was obtained but with increased matrix interference, so MeOH was used for further extractions.

We then tested the method on an ancient marine sediment, i.e. a sample from a core from the Murray Canyons area, offshore southeast Australia and dated at ca. 20.4 ka (Gingele and De Deckker, 2005). The area received dust from nearby Murray–Darling River Basin and thus potentially carried vegetation fire signals. Indeed, we detected lVG (243 pg g^{-1} sediment; Fig. 1c), showing that our method is also suitable for analyzing fossilized LVG present in marine sediments. Future research should investigate the use of deuterated LVG as an internal standard for improved quantification using HPLC-MS^2.

4. Conclusions

We have developed a novel HPLC-MS^2 method for analysis of levoglucosan in soils and sediments. The method is relatively rapid

as it does not require extensive sample clean up or derivatization, and requires less sample material, enabling rapid generation of high resolution records of levoglucosan, and thus biomass burning, from sedimentary archives.

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