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Technical note

Development of an in situ derivatization technique for rapid analysis of levoglucosan and polar compounds in atmospheric organic aerosol

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HIGHLIGHTS

- New in situ silylation and thermal desorption GCMS method for levoglucosan.
- Good comparison with high-volume injection GCMS for $PM_{2.5}$ filter samples.
- Levoglucosan peaks in nighttime and early morning in wintertime in Fresno, CA.

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ABSTRACT

A novel thermal desorption gas chromatography mass spectrometry (TD-GCMS) technique was developed for the analysis of levoglucosan and other polar compounds in atmospheric organic aerosol. The method employs an in situ derivatization to add tri-methylsilyl groups to alcohol functional groups on simple carbohydrates, like levoglucosan and sterols. The new method was then demonstrated on a set of 40 filter samples collected in Fresno, CA. The results from the in situ silylation TD-GCMS method were compared, using levoglucosan, with a solvent extraction, high-volume injection GCMS method resulting in an $r^2 = 0.91$.

1. Introduction

There is a great need to further characterize the carbonaceous fraction of atmospheric aerosols to better understand the impacts on human health and global climate forcing. The chemical composition of the carbonaceous fraction influences a variety of physical properties that determine how atmospheric aerosols will impact human health and the environment. Routine measurements of organic carbon and elemental carbon (OC and EC), along with the measurement of other bulk particulate matter constituents (sulfate ions, nitrate ions, ammonium ions, crustal species, and trace metals) are not sufficient to properly understand the origin, dynamics, and potential impact of atmospheric aerosols. Molecular markers are often used to estimate source contributions, and they can indicate whether aerosol is dominated by primary or secondary organic carbon. Levoglucosan is a widely used molecular marker for biomass burning, and it has also been utilized to characterize the polarity of atmospheric OC (Boreddy et al., 2014; Crilley et al., 2015; Fu et al., 2010; Gao et al., 2011; Nguyen et al., 2014; Offenberg et al., 2011; Scaramboni et al., 2015; Yttri et al., 2014, 2015). While levoglucosan has become a routine measurement, there is continued interest in optimizing the analytical method for time, consumable reduction, and minimization of detection limit (Yttri et al., 2015).

Gas chromatography mass spectrometry (GCMS) is still the most common analytical technique employed for levoglucosan measurement. To this end, there is a great need to maximize the abilities of GCMS for analysis of levoglucosan and to find analytical strategies that reduce resource use for this measurement. This can be accomplished by optimizing solvent extraction techniques, e.g.

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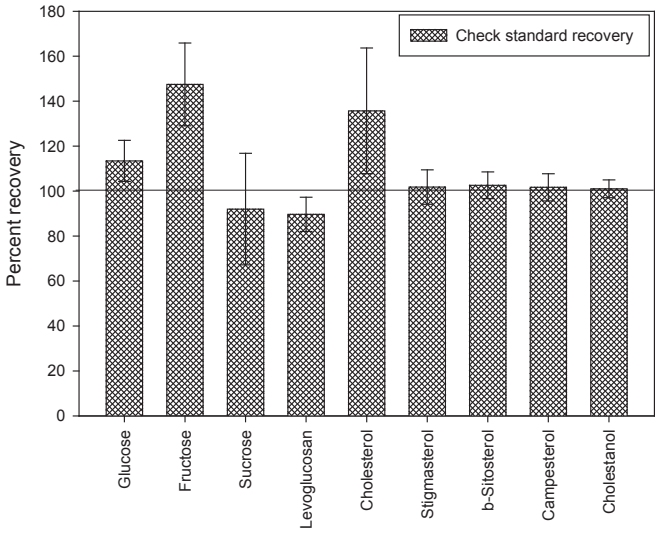

Fig. 1. Check standard average recovery with error bars representing the standard error (n = 12).

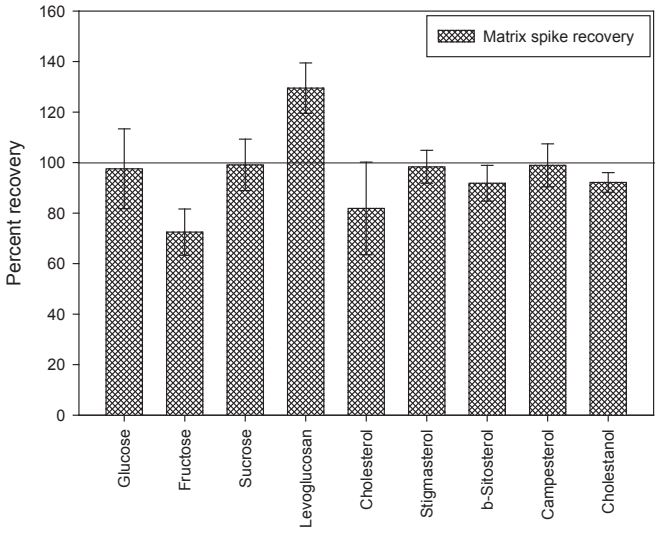

Fig. 2. Matrix spike average recovery with the error bars representing the standard error (n = 5). Matrix spikes use standards spiked directly onto ambient samples (Fresno project) to examine target recovery in an ambient PM matrix.

using accelerated solvent extraction (ASE) (Clark et al., 2015); and by maximizing sample injection into the GCMS, i.e. programmable temperature vaporization GCMS (PTV-GCMS) (Dutton et al., 2009; von Schneidemesser et al., 2008). In parallel, non-solvent extraction techniques have been pioneered. Thermal desorption GCMS (TD-GCMS) has previously been demonstrated for non-polar organic molecular markers (Sheesley et al., 2007) and in situ methylation TD-GCMS has been demonstrated for organic acid molecular markers (Sheesley et al., 2010). This TD-GCMS method has now been expanded to include silylation derivatization for analysis of levoglucosan. The novel protocol described here has realized three important advances in GCMS analysis of levoglucosan that build on the TD-GCMS protocol:

1) Elimination of costly solvents for extraction
2) Significant reduction in operator time compared to solvent extraction
3) Minimization of required sample

a) Lower ambient detection, 1–7 μg OC used in analysis compared to 200–400 μg OC for small volume injection GCMS and 9–60 μg OC for high-volume injection.

The use of TD-GCMS reduces the resources and costs of particulate matter organic compound speciation by a factor of 5–10 when compared to traditional soxhlet or sonication-based solvent extraction, with a reduction in total costs of roughly 50% over current solvent-based techniques (Sheesley et al., 2010, 2008). These reduced costs are predominately associated with the time-consuming solvent extraction process, concentration steps, and associated glassware cleaning necessary for trace organics analysis. In this study, we present a new method for the rapid analysis of levoglucosan, sterols, and simple carbohydrates using in situ silylation combined with TD-GCMS using electron ionization. Method validation is reported, including analysis of duplicate ambient samples, matrix spikes (standard spiked onto ambient samples to assess recovery) and check standards (standards run between calibration curves to assess the stability of the instrument). In addition, the method was demonstrated on ambient samples collected in Fresno, CA during February. 2007, and these results are compared to parallel ASE extraction and analysis by PTV-GCMS. Levoglucosan was measured in all 40 ambient samples. Additional simple carbohydrates and sterols were included in the method validation, but were not consistently measured in the ambient study. Method intercomparison for all 40 of the Fresno samples demonstrates compatibility between solvent extraction and TD-GCMS analysis of levoglucosan. The filter-based ambient samples (6 h) also demonstrate the utility of these analytical improvements in bettering temporal resolution of levoglucosan measurements.

2. Methods

2.1. In situ silylation TD-GCMS method

A Markes International Thermal Desorption Unit (Model M-10140) (Foster City, CA, USA) coupled with an Agilent Technologies 5973 GCMS was used for the sample analysis. A single filter punch (1.0 cm^2) was used in the analysis, which represented 1–7 μg OC. Glassware was baked at 550 °C and solvent rinsed before use. Forty microliters of 1:5 diluted BSTFA silylation reagent (N,O-bis(-trimethylsilyl)trifluoroacetamide plus trimethylchlorosilane from Supelco) was added to a clean vial, which had a needle fitted into the cap to suspend the filter punch. The filter sample was placed on the needle and then spiked with an isotopically-labeled internal standard containing ^{13}C–labeled levoglucosan, deuterated glucose, and deuterated cholesterol. After the vial was closed, the filter was wetted with the diluted reagent and the vial was heated at 70 °C for 1 h. The filter punch was not allowed to dry. Finally, the filter was removed from the vial, inserted into a glass desorption tube, and placed into the autosampler. The sample tube was ramped to 360 °C for 20 min to desorb the compounds of interest from the filter. A high-boiler quartz focusing trap, designed for analysis of n-hexane to n-tetracontane semi-volatile organic compounds (0 °C), was used to focus the sample before the temperature was increased to 360 °C again and desorbed onto the GC column; this focusing step concentrated the analytes desorbed from the filter into a smaller volume of vapor, which improved the GCMS detection limit.

A four point calibration curve was run at the start of each sample set. The quantification standard included levoglucosan, glucose, sucrose, fructose, and five sterols, which were used to quantify the corresponding compounds within the filter samples. The quantification standards were spiked onto a blank filter punch and the solvent was allowed to evaporate before undergoing the derivatization procedure detailed above for the particulate matter samples.