Results of an interlaboratory comparison of analytical methods for quantification of anhydrosugars and biosugars in atmospheric aerosol

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HIGHLIGHTS

- An intercomparison study was performed in 10 Italian laboratories for quantifying sugars in PM.
- Gas and Liquid chromatography and NMR methods were used for analysis of 26 ambient and 3 synthetic PM filters.
- Different separation and detection systems yielded comparable results for most of the samples.
- Low interlaboratory variability (RSD% from 25% to 46%) and good accuracy (ε% within ±20%) were found.

GRAPHICAL ABSTRACT
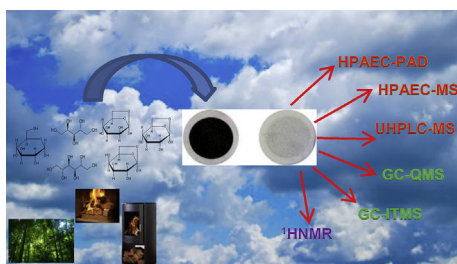
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ABSTRACT

An interlaboratory comparison was performed to evaluate the analytical methods for quantification of anhydrosugars — levoglucosan, mannosan, galactosan — and biosugars — arabitol, glucose and mannitol — in atmospheric aerosol. The performance of 10 laboratories in Italy currently involved in such analyses was investigated on twenty-six PM (particulate matter) ambient filters, three synthetic PM filters and three aqueous standard solutions.

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An acceptable interlaboratory variability was found, determined as the mean relative standard deviation (RSD%) of the results from the participating laboratories, with the mean RSD% values ranging from 25% to 46% and decreasing with increasing sugar concentration. The investigated methods show good accuracy, evaluated as the percentage error (ε%) related to mean values, since method biases ranged within ±20% for most of the analytes measured in the different laboratories.

The detailed investigation (ANOVA analysis at $p < 0.05$) of the contribution of each laboratory to the total variability and the measurement accuracy shows that comparable results are generated by the different methods, despite the great diversity in terms of extraction conditions, chromatographic separation - more recent LC (liquid chromatography) and EC (exchange chromatography) methods compared to more widespread GC (gas chromatography) - and detection systems, namely PAD (pulsed amperometric detection) or mass spectrometry.

1. Introduction

There is a general consensus that emissions from residential wood combustion strongly impact air quality, especially during the winter seasons, when the domestic burning of wood logs, briquettes, chips and pellets represents an important renewable energy source. In fact, biomass combustion in domestic appliances has been demonstrated to contribute significantly to emissions of the total $PM_{2.5}$ and PM_{10} and also to contain numerous toxic/carcinogenic components with a potentially high impact on human health (Calvo et al., 2013; Perrone et al., 2013; Xu et al., 2015). Therefore, there are increasing efforts in the monitoring of the contribution of such emissions, that is based on the quantification of the chemical tracers for biomass burning useful to estimate both open and residential biomass combustion to fine particle concentrations. The key tracer is levoglucosan - with minor quantities of its isomers mannosan, galactosan - as primarily produced during biomass combustion as the pyrolytic decomposition product of cellulose and hemicellulose (Calvo et al., 2016; Herich et al., 2014; Kourtchev et al., 2011; Puxbaum et al., 2007). An additional input of levoglucosan - and minor quantities of mannosan — to the atmosphere may be the burning of lignites in regions where brown coal is utilized as a domestic fuel (Fabbri et al., 2009). Despite regulations being needed to increase the incentives to take these compounds into consideration, tools that facilitate accurate monitoring of them are also important. Although several procedures have been applied to analyze sugars in atmospheric aerosol, the absence of a standardized method leaves still open the question of whether results generated by a given method accurately depict the true concentration of each sugar in the aerosol and whether the results from various methods are comparable (Kourtchev et al., 2011; Schkolnik and Rudich, 2006; Yttri et al., 2015).

Because NIST Standard Reference Materials of Fine Particulate Matter are available only for three anhydrosugars (i.e., SRM2786 e SRM2787) and matrix effects caused by non-target background interferences may lead to report inaccurate concentrations, interlaboratory comparison studies are the best means to assess the comparability of the reported data on a compound-by-compound basis (Lundstedt et al., 2014; Vanderford et al., 2014; Yttri et al., 2015).

The present paper describes an interlaboratory study with the objective to compare the performance of 10 laboratories for quantifying sugars in ambient aerosol using the most common methods in ongoing research and monitoring efforts, as reported in the scientific literature so far. They are gas chromatographic methods, that have been the well-established for many years (Fabbri et al., 2008; Hsu et al., 2007; Pashynska et al., 2002; Pietrogrande et al., 2013), and liquid chromatographic methods, that were more recently developed and are actually gaining attention (Engling et al., 2006; Caseiro et al., 2007; Piazzalunga et al., 2010; Piot et al., 2012; Yttri et al., 2015; Barbaro et al., 2015). The investigated methods differ to a large extent with respect to crucial parameters, such as extraction procedure and derivatization agent, chromatographic separation and detection systems, which are variously combined. This adds additional strength to any conclusion to be drawn from the study.

In order to investigate the possible effect of unknown interferences in the complex PM matrix, the study was performed on different sample types, i.e., aqueous standard solutions, synthetic PM filters and PM ambient filters.

2. Experimental section

2.1. Analytical methods used by the participating laboratories

Ten laboratories located in different cities in Italy participated in the current intercomparison exercise. They adequately represent the most widespread employed methods for analysis of sugars in atmospheric aerosol (Schkolnik and Rudich, 2006; Yttri et al., 2015). A brief overview of the various analytical methods is given in Table 1, including information about the instrument used for separation and detection of the analytes, the solvent(s) and experimental condition used for extraction and whether analytes derivatization was applied.

Among the wide variety of the analytical procedures used in this study, each technique shows different advantages and disadvantages (Schkolnik and Rudich, 2006). GC-MS (lab GC-MS1 and GC-MS2, Table 1) is the most widespread technique for analysis of anhydrosugars in atmospheric samples (Medeiros et al., 2006; Fabbri et al., 2008; Hsu et al., 2007; Pashynska et al., 2002; Pietrogrande et al., 2013; Yttri et al., 2015). The main advantage of this technique is the good selectivity related to high efficiency of capillary GC columns and specificity of m/z values in mass spectra. However, due to the polar nature of the sugars, a preliminary derivatization step of the hydroxyl groups is needed to increase the volatility and thermal stability of the analytes and to reduce their surface interactions. N,O-bistrimethylsilyltrifluoroacetamide (BSTFA) in combination with trimethylchlorosilane (TCMS) is one of the most commonly used reagents (Hsu et al., 2007; Fabbri et al., 2008; Pietrogrande et al., 2013). This step makes the sample preparation labor-intensive and volume expensive, since it requires serial extraction with one or more organic solvents and evaporation to dryness of the solvent (Pashynska et al., 2002; Schkolnik and Rudich, 2006; Pietrogrande et al., 2013). As alternative, HPLC technique does not require any derivatization step, but it needs specific stationary phases playing selectivity for sugars separation.