Intercomparison of chromatographic methods used for quantification of levoglucosan in ambient aerosol filters

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The quantification in atmospheric aerosol of monosaccharide anhydrides, levoglucosan, galactosan and mannosan, as major constituents of biomass burning aerosol particles, is commonly used to study the influence of residential wood and pellet burning, agricultural waste burning and wildfire emissions (BB) on ambient air quality. This work investigates the comparability of the two most commonly used methods for analysis of such tracers in PM samples, namely anion-exchange chromatography (IC coupled with amperometric detection) and gas chromatography coupled to Mass Spectrometry (GC/MS).

The study was performed on ambient PM_{10} and $PM_{2.5}$ quartz fiber filter samples collected at urban background sites in Milan (Lombardia, Northen Italy) during winter 2014, that are representative for BB particles originating from residential wood burning.

Portions (a 1.5 cm^2 punch) of the same filter were submitted to IC analysis in Milan and Trento and to GC/MS determination in Ferrara laboratories. Other than separation/detection, the two methods mainly differ to a large extent with respect to extraction procedure, as a simple extraction with water precedes IC analysis, while solvent extraction with methanol/dichloromethane mixture followed by trimethylsilylation derivatisation is required for the GC/MS procedure (Pietrogrande *et al.*, 2013, 2014).

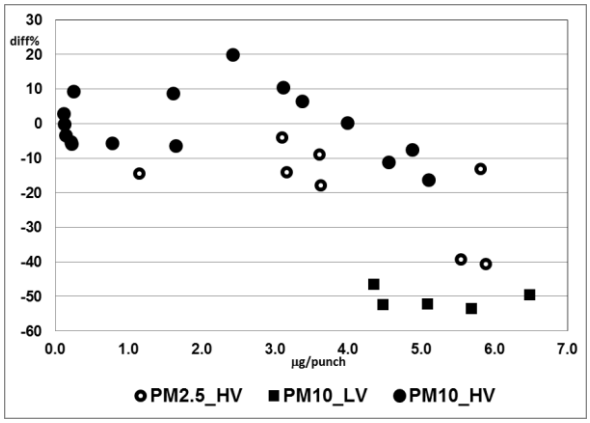

Figure 1. Comparison between GS/MS and IC measurements of levoglucosan concentration.

The comparability of the two methods was expressed by the mean percentage variation between the GS/MS and IC results (diff%) of each analyzed sample. Figure 1 reports this comparison for levoglucosan as a function of analyte concentration (expressed as levoglucosan load on sampled filter, µg/punch).

For all the analytes a good comparability between the two procedures was found, as described by diff% values within the range ±20% for the investigated samples. The exceptions are some negatively biased GC/MS results (diff% ≥ 40%) obtained for highly loaded filters, containing more than 4.5 µg of levoglucosan on the analyzed punch. Under the sampling procedures used, these samples correspond to more than 0.9 µg m^{-3} of levoglucosan in the sampled air, in combination with large amount of PM_{10} (≥ 50 µg m^{-3}) or $PM_{2.5}$ (≥ 30 µg m^{-3}). For this reason, this behavior may be likely ascribed to the limited solubility of sugars in methanol/dichloromethane mixture that prevents the unbiased analyte extraction.

These adverse sampling conditions are typically found in PM samples collected during wintertime in Lombardia, where residential biomass burning is the major source of PM and ambient levoglucosan concentration can reach values well above 1 µg m^{-3} in combination with high level of PM_{10} and/or $PM_{2.5}$ concentration (Piazzalunga, *et al.*, 2011, Giannoni, *et al.*, 2012).

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