



This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

# Quantification of levoglucosan and its isomers by High Performance Liquid Chromatography – Electrospray Ionization tandem Mass Spectrometry and its applications to atmospheric and soil samples

C. Piot<sup>1,2</sup>, J.-L. Jaffrezo<sup>2</sup>, J. Cozic<sup>2</sup>, N. Pissot<sup>1</sup>, I. El Haddad<sup>3</sup>, N. Marchand<sup>3</sup>, and J.-L. Besombes<sup>1</sup>

<sup>1</sup>Université de Savoie, LCME, Le Bourget du lac, France

Received: 17 March 2011 – Accepted: 7 July 2011 – Published: 18 July 2011

Correspondence to: C. Piot (christine.pirot@univ-savoie.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



<sup>2</sup>Université Joseph Fourier-CNRS, UMR5183, LGGE, St Martin d'Hères, France

<sup>3</sup>Universités Aix-Marseille I, II et III-CNRS, UMR6264, LCP, Marseille, France

Received: 17 March 2011 – Accepted: 7 July 2011 – Published: 18 July 2011

Correspondence to: C. Piot (christine.piot@univ-savoie.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

**Levoglucosan and its  
isomers by  
LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## Abstract

The determination of atmospheric concentrations of levoglucosan and its two isomers, unambiguous tracers of biomass burning emissions, became even more important with the development of wood as renewable energy for domestic heating. Many researches 5 demonstrated the increase during recent years of atmospheric particulate matter load due to domestic biomass combustion in developed countries. Analysis of biomass burning tracers is traditionally performed with Gas Chromatography-Mass Spectrometry (GC-MS) technique after derivatization and requires an organic solvent extraction. A simpler and faster technique using Liquid Chromatography – Electrospray Ionisation 10 – tandem Mass Spectrometry (LC-ESI-MS/MS) was optimized for the analysis of levoglucosan, mannosan and galactosan isomers after an aqueous extraction. This technique allows a good separation between the three compounds in a very reduced time (runtime  $\sim$ 5 min). LOD and LOQ of this method are  $30 \mu\text{g l}^{-1}$  and  $100 \mu\text{g l}^{-1}$  respectively, allowing the use of filters from low-volume sampler (as commonly used in 15 routine campaigns). A comparison of simultaneous levoglucosan measurements by GC-MS and LC-ESI-MS/MS for about 50 samples coming from different types of sampling sites and seasons was realized and shows very good agreement between the two methods. Therefore LC-ESI-MS/MS method can be used as an alternative to GC-MS particularly for measurement campaigns in routine where analysis time is important 20 and detection limit is reduced. This paper shows that this method is also applicable to other environmental sample types like soil.

## 1 Introduction

A growing number of scientific studies have recently focused on the apportionment of biomass burning emissions in ambient aerosol (Zheng et al., 2002; Puxbaum et al., 25 2007; Gaeggeler et al., 2008; Caseiro et al., 2009). This primary source emits high amounts of organic aerosol (OA) and can largely contribute to the OA mass of particulate matter (PM) in winter. For example in Europe, biomass burning contributions to OA

AMTD

4, 4539–4560, 2011

## Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶|](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

focused on lignites. However, these studies seem to indicate that monosaccharide anhydrides could be used as proxies for the detection of the impact of biomass burning events in many types of matrices.

Analysis of molecular markers is traditionally performed using Gas Chromatography-Mass Spectrometry (GC-MS) technique after organic solvent extraction and derivatization steps (Bergauff et al., 2008). Widely used for the chemical characterization of atmospheric aerosol, this method is also used for the analysis of soil samples (Otto et al., 2006; Simoneit et al., 2004). Even though the reliability of this approach is demonstrated in several studies, it requires intensive and expensive sample preparation. In addition, the derivatization step usually based on a silylation reaction prevents the analysis of aqueous samples. Recently, other analytical methods without derivatization step were developed for monosaccharide anhydrides quantification using High Performance Liquid Chromatography (HPLC) coupled with various detectors, including pulsed amperometric detection (PAD) (Engling et al., 2006; Caseiro et al., 2007), aerosol charge detection (ACD) (Dixon and Baltzell, 2006), mass spectrometry (MS) (Dye and Yttri, 2005; Wan and Yu, 2006; Gambaro et al., 2008; Saarnio et al., 2010) and Electrospray Ionisation-tandem Mass Spectrometry (ESI-MS/MS) (Palma et al., 2004). Ion-exclusion chromatography coupled with a spectroscopic detection was also used to analyse directly rainwater (Schkolnik et al., 2005) and microchip capillary electrophoresis coupled with pulsed amperometric detection allows a quick analysis of levoglucosan (Garcia et al., 2004). However, only few papers have compared the analytical performance of these methods with the more widely used GC-MS technique (Engling et al., 2006; Schkolnik et al., 2005).

In this study, we present a new method based on coupling HPLC and Electrospray Ionisation-tandem Mass Spectrometry (ESI-MS/MS), which provides an appropriate separation of the monosaccharide anhydride isomers, a sensitive detection, and a fast and inexpensive analysis. Tandem Mass Spectrometry allows a better selectivity of compounds by selecting daughter ion characteristics of the studied compounds (levoglucosan and its isomers).

This method allows the analysis in the aqueous phase and is therefore applicable to a wide variety of environmental samples including atmospheric aerosol, soil and water (rain, snow, ice) samples. Atmospheric samples from different sites and seasons were simultaneously analyzed with this direct method and with the derivatization-GC-MS method in order to compare their analytical performances. The application of the HPLC-ESI-MS/MS method (called LC-MS) to levoglucosan quantification in soil sample is also presented.

## 2 Material and methods

### 2.1 Reagents and materials

Authentic standards used in this study include levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) 99.0 % (CAS 498-07-7, Sigma-Aldrich, Steinheim, Germany), mannosan (1,6-anhydro- $\beta$ -D-mannopyranose) (CAS 14168-65-1, Carbosynth, Compton, U.K.) and galactosan (1,6-anhydro- $\beta$ -D-galactopyranose) (CAS 644-76-8, TRC, Toronto, Canada). Standard solutions, sample extraction, and mobile phase solutions were prepared with ultrapure water (Purelab Ultra system, Elga, High Wycombe, UK). Stock solutions at 10 g l<sup>-1</sup> were prepared by dissolving 1.00 g of each compound in 100 ml of ultrapure water. These solutions were stored in amber glass bottles (SCHOTT® Duran®) at 4 °C. Sodium hydroxide solutions for the mobile phase were prepared from a 50 % (w/w) NaOH solution (J.T. Baker). Ultrapure water was degassed with He before NaOH addition in order to limit carbonate formation.

### 2.2 Sample collection and LC-MS extraction

Atmospheric particulate matter of less than 10 µm and 2.5 µm diameter (PM<sub>10</sub>, and PM<sub>2.5</sub>, respectively) were collected onto QM-A quartz fiber filters (Whatman) in a high-volume sampler (flow rate 30 m<sup>3</sup> h<sup>-1</sup>) with collection times of 12 or 24 h. Samples were

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

collected in two urban background sites in France: “Les Frênes” in Grenoble and “Cinq Avenues” in Marseille, during autumn to winter 2009 and summer 2008, respectively, during the FORMES program (Favez, 2010; El Haddad, 2011). After collection, samples were stored at  $-20^{\circ}\text{C}$ , with filters sealed in aluminum foil and polyethylene bags.

5 Soil samples were collected in the top soil horizon (between two and five cm depth) located under a charcoal burning two days after the end of the combustion, in the karstic Vercors massif (French Alps). After collection, they were air dried at room temperature and sieved at 2 mm.

Appropriate atmospheric sample fractions (3 to 12  $\text{cm}^2$ ) and soil sample fractions 10 of 5 g were extracted with 15 ml and 5 ml, respectively, of ultrapure water with a vortex agitation during 20 min. Longer agitation and ultrasonic agitation were also tested. In order to evaluate extraction recoveries of the two extraction methods (ultrasonic or 15 vortex agitation), blank Whatman QM-A filters were spiked in triplicate with a standard solution containing the three monosaccharides in aqueous solvent at low, medium and high concentrations (100, 500, and 1000  $\mu\text{g l}^{-1}$ ). They were air dried at room temperature in order to evaporate the aqueous solvent. The results are discussed in Sect. 3.1.

Just before the analysis, extracts were further filtered using Acrodisc® filters (Pall, Gelmann) with a porosity of 0.22  $\mu\text{m}$  previously rinsed with 40 ml of ultrapure water. Soil samples extracts were previously filtered using pleated filter cellulose paper.

## 20 2.3 LC-MS analysis

Sample was analyzed using High Performance Liquid Chromatography – Electrospray Ionisation – tandem mass spectrometry (HPLC-ESI-MS2) like presented by Piot et al. (2009). Liquid chromatography is performed with a Dionex pump (model DX500) mounted with Peek and vacuum degasser. Sample is injected by a 449  $\mu\text{l}$  injection 25 loop. The separation is carried out at room temperature (about  $20^{\circ}\text{C}$ ) using a Carbopac PA-1 anion-exchange analytical column (250 mm  $\times$  4 mm, Dionex) coupled with a Carbopac PA-1 guard column (50 mm  $\times$  4 mm, Dionex) like in Caseiro et al. (2007). Elution is achieved in isocratic mode at  $1.2 \text{ ml min}^{-1}$  with 0.5 mM sodium hydroxide solution.

Columns are flushed and equilibrated between two samples with an elution gradient between 0.5 and 3 mM sodium hydroxide at a  $1.2 \text{ ml min}^{-1}$  flow rate (run time: 9 min). During this step, the mobile phase is not injected into the MS. Columns are washed overnight (after approximately 20 samples) with an elution gradient between 0.5 and 200 mM sodium hydroxide at a  $0.5 \text{ ml min}^{-1}$  flow rate (run time: 15 h).

5 A micrometric split valve is used to reduce the flow injected to the MS at  $0.8 \text{ ml min}^{-1}$ . The analytical detector is an Electrospray Ionization Ion Trap MS (LCQ Fleet MS, Thermo Fisher Scientific). Detection is achieved in the negative ion mode like in Gambaro et al. (2008) with a *m/z* 161 trap isolation. Parameters are optimized for the best 10 Collision Induced Dissociation (CID) efficiency with selective current in *m/z* 101 and *m/z* 113, characteristic of daughter ions of levoglucosan and its two isomers. Instrumental conditions are reported in Table 1. Chromatogram integration is realized on the selective current:  $m/z 101 \pm 0.5 + 113 \pm 0.5$ .

15 Calibration is performed twice, at the beginning of the analysis sequence and at the end of the sequence, with standard solutions containing the three monosaccharides at 100, 500, and  $1000 \mu\text{g l}^{-1}$ . Samples and standard solutions are injected twice for each analysis.

## 2.4 GC-MS analysis

20 Standards and atmospheric samples are simultaneous analyzed by GC-MS as described in El Haddad et al. (2009). Authentic standard solutions were prepared in acetone and stored at  $4^\circ\text{C}$ . Briefly, sample fractions are extracted with a dichloromethane/acetone mix (1:1 v/v) using an Accelerated Solvent Extractor (ASE 200, Dionex) and reduced to a volume of 1 ml. A 100  $\mu\text{l}$  extract fraction is trimethylsilylated with 100  $\mu\text{l}$  of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1 % 25 trimethylchlorosilane (TMCS) for two hours at  $50^\circ\text{C}$  before GC-MS analysis. Quantification is performed using selected ion current peak areas (204 for levoglucosan and mannosan and 217 for galactosan) and calibration curves are established with authentic standards and a deuterated levoglucosan internal standard. Calibration was

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

checked every 10 samples and is performed with 8 levels of concentration between 2 and 400  $\mu\text{g l}^{-1}$ .

### 3 Results and discussion

#### 3.1 Methods performance

5 The elution conditions used in the LC-MS method allow the detection of the three monosaccharides in less than 6 min with a very good separation (Fig. 1a). The levoglucosan retention time is about 2.3 min followed successively by mannosan, and galactosan. The chromatogram shows a high resolution (Rs: peak resolution) between the three peaks (Rs = 1.25 for levoglucosan and mannosan and Rs = 1.65 for mannosan and galactosan) in a very reduced time (runtime  $\sim$ 5 min). However, this method allows only the analysis of levoglucosan and its two isomers. All analytical performance and linear regression parameters for LC-MS calibration are presented in Table 2. Limit of detection (LOD) of the analytical method presented in this paper (3 times the standard deviation of the blank) is 30  $\mu\text{g l}^{-1}$  and the limit of quantification (LOQ) (10 times the standard deviation of the blank) is 100  $\mu\text{g l}^{-1}$  (Table 2). The analytical concentration range was 20 to 2000  $\mu\text{g l}^{-1}$ .

15 Calibration curves systematically show  $R^2$ -values above 0.996 for the three compounds. Analytical reproducibility, evaluated by the relative standard deviation (RSD) between five successive injections of the same standard solution at concentrations of 500 and 1000  $\mu\text{g l}^{-1}$ , ranges between 5 to 10 %. In conditions of extraction allowing 20 two injections and the analysis of a sample, mass LOD is 60 ng.

25 The analysis of levoglucosan by GC-MS is traditionally conducted after an organic solvent extraction using dichloromethane (Simoneit et al., 1999) or mixture of dichloromethane and methanol (Simoneit, 2002). In the case of HPLC analysis, some studies used a water extraction assisted by ultrasonic or short vortex agitation to extract saccharides because of their high solubility in water (Caseiro et al., 2007; Engling

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶|](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶|](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

### 3.2 Comparison of LC-MS and GC-MS analysis to atmospheric applications

Parallel analyses were conducted by LC-MS and GC-MS methods on the same fifty atmospheric samples (a different fraction of each sample was analyzed with each method). Samples were collected during different seasons between summer 2008 and 5 winter 2009 in two urban background sites located in Marseille and Grenoble, the second and the sixteenth most populated city in France respectively. Sampling of  $360\text{ m}^3$  and  $720\text{ m}^3$  were collected with High-Volume samplers. Concentrations were corrected by extraction efficiencies. Levoglucosan concentrations covered a wide range from 4 to  $3200\text{ ng m}^{-3}$  and concentrations found are in the same range as previous measurements reported in Europe. For instance, Caseiro et al. (2009) measured concentrations 10 ranging from 20 to  $400\text{ ng m}^{-3}$  of levoglucosan in Austrian Regions and Puxbaum et al. (2007) measured 0.3 to  $1651\text{ ng m}^{-3}$  in CARBOSOL sites.

Comparison between the two methods was only made for levoglucosan since concentrations of the other monosaccharide anhydrides (mannosan and galactosan) were 15 lower than the detection limit for too many samples. Results show an excellent agreement between the LC-MS and GC-MS methods, with a slope of almost unity, within the uncertainty of the measurement, and  $R^2$ -values of 0.94 (Fig. 2). This comparison validates the LC-MS method versus the more traditional GC-MS method for the analysis of atmospheric levoglucosan. With a lower detection limit for atmospheric analysis 20 and faster sample treatment, LC-MS method represents a very good alternative to the widely used GC-MS method. With this method, quantification of levoglucosan could be achieved in low-volume sampling conditions and for field campaigns with many samples.

Several such studies are in progress in our labs in different environment type (rural, 25 urban, alpine sites...), including collections with low volume samplers ( $1\text{ m}^3\text{ h}^{-1}$ ) for week-long sampling, and for a year-long survey of eight urban background sites in the Rhône-Alpes Region (Piot, 2011; Piot et al., 2011) where measured levoglucosan concentrations range between  $4\text{ ng m}^{-3}$  (in summer) and  $1000\text{ ng m}^{-3}$  (in winter).

AMTD

4, 4539–4560, 2011

### Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



### 3.3 Other environmental samples analysis

The use of aqueous solvent for levoglucosan extraction in the LC-MS method allows to consider the analysis of monosaccharide anhydrides in many environmental matrices. Levoglucosan and its two isomers were analyzed by the LC-MS method in 5 soil samples collected under wood fire combustion (2 to 5 cm depth) two days after the end of a combustion performed to produce charcoal. Extraction with Soxhlet and dichloromethane, and analyses using GC-MS were performed but no monosaccharide anhydrides were observed in these analytical conditions. Water extraction (5 g of soil extract with 5.0 ml of water during 20 min of short vortex agitation) was undertaken 10 and followed by LC-MS analysis. In these conditions, concentrations of 10.0, 1.5 and 0.6  $\mu\text{g g}^{-1}$ , were measured for levoglucosan, mannosan and galactosan, respectively, highlighting a noteworthy impact of fire combustion on soil. Otto et al. (2006) have analyzed charred pine forest surface soil samples in Canada by GC-MS after organic 15 solvent extraction and have measured levoglucosan, mannosan and galactosan concentrations of 1.0, 0.6, and 0.3  $\mu\text{g g}^{-1}$ , respectively. Simoneit et al. (2004) measured levoglucosan concentrations of less than 0.1  $\mu\text{g g}^{-1}$  in soil or soil dust weakly impacted by biomass burning. Thus, data reported in the literature are much lower than concentrations measured in this study. This may be related to the type of soil samples, or maybe due to a better efficiency of water extraction than organic solvent extraction for 20 soil samples. Additional tests would be necessary to compare aqueous and organic solvent extraction methods but test samples of soil with certified levoglucosan concentrations do not exist in order to quantify the extraction efficiency. However, the analysis of levoglucosan in soil, easily achievable with the LC-MS method with a low detection limit, is a promising way that can allow to evaluate the impact of forest fires in such 25 environmental archives.

### Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## 4 Conclusions

Levoglucosan concentrations of atmospheric samples obtained with two independent methods (LC-MS and GC-MS) were compared and present extremely good correlation for a wide range of concentrations. This shows the validity of the LC-MS measurements. Whereas the GC-MS allows the detection of a large number of compounds and can handle large atmospheric concentration range, the LC-MS method allows only to measure water-soluble compounds like levoglucosan. Nevertheless, analytical performances are better for the LC-MS method (lower LOD, better recovery) than for the GC-MS method. Moreover one of the main advantages of the LC-MS method is its rapidity, allowing the processing of large sets of samples in order to obtain data for this biomass burning marker in large field campaigns. In fact, LC-MS allows the analysis of monosaccharide anhydrides in less than five min with a shorter time of sample preparation using a cheaper and very simple extraction technique with less impact on the environment. Finally, the extraction method used in LC-MS can be applied to many environmental types, as for example soil whose moisture does not allow organic solvent extraction.

*Acknowledgements.* The authors would like to thank staffs from ASCOPARG and EDYTEM for their support during the field campaigns and Bastien Mettra for his contribution to this work. C. Piot thanks the Region Rhône-Alpes for her PhD grant.

## 20 References

Bergauff, M., Ward, T., Noonan, C., and Palmer, C. P.: Determination and evaluation of selected organic chemical tracers for wood smoke in airborne particulate matter, *Int. J. Environ. Anal. Chem.*, 88, 473–486, 2008.

Caseiro, A., Marr, I. L., Claeys, M., Kasper-Giebl, A., Puxbaum, H., and Pio, C. A.: Determination of saccharides in atmospheric aerosol using anion-exchange high-performance liquid chromatography and pulsed-amperometric detection, *J. Chromatogr. A*, 1171, 37–45, 2007.

AMTD

4, 4539–4560, 2011

## Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶|](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Caseiro, A., Bauer, H., Schmidl, C., Pio, C. A., and Puxbaum, H.: Wood burning impact on PM<sub>10</sub> in three Austrian regions, *Atmos. Environ.*, 43, 2186–2195, 2009.

Dixon, R. W. and Baltzell, G.: Determination of levoglucosan in atmospheric aerosols using high performance liquid chromatography with aerosol charge detection, *J. Chromatogr. A*, 1109, 214–221, 2006.

Dye, C. and Yttri, K. E.: Determination of Monosaccharide Anhydrides in Atmospheric Aerosols by Use of High-Performance Liquid Chromatography Combined with High-Resolution Mass Spectrometry, *Anal. Chem.*, 77, 1853–1858, doi:10.1021/ac049461j, 2005.

El Haddad, I., Marchand, N., Dron, J., Temime-Roussel, B., Quivet, E., Wortham, H., Jaffrezo, J. L., Baduel, C., Voisin, D., Besombes, J. L., and Gille, G.: Comprehensive primary particulate organic characterization of vehicular exhaust emissions in France, *Atmos. Environ.*, 43, 6190–6198, 2009.

Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett Jr, J. L., Day, D. E., Malm, W. C., Lincoln, E., Min Hao, W., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, *Atmos. Environ.*, 40, 299–311, 2006.

Fabbri, D., Marynowski, L., Fabińska, M. J., Zatonī, M., and Simoneit, B. R. T.: Levoglucosan and Other Cellulose Markers in Pyrolysates of Miocene Lignites: Geochemical and Environmental Implications, *Environ. Science Technol.*, 42, 2957–2963, doi:10.1021/es7021472, 2008.

Favez, O., Cachier, H., Sciare, J., Sarda-Estève, R., and Martinon, L.: Evidence for a significant contribution of wood burning aerosols to PM2.5 during the winter season in Paris, France, *Atmos. Environ.*, 43, 3640–3644, 2009.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., and D'Anna, B.: Intercomparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France), *Atmos. Chem. Phys.*, 10, 5295–5314, doi:10.5194/acp-10-5295-2010, 2010.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Wood Types Grown in the Midwestern and Western United States, *Environ. Eng. Sci.*, 21, 387–409, doi:10.1089/109287504323067021, 2004.

Fraser, M. P. and Lakshmanan, K.: Using Levoglucosan as a Molecular Marker for the Long-

## Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, *J. Geophys. Res.*, 112, D23S05, doi:10.1029/2006jd008114, 2007.

Saarnio, S., Teinilä, K., Aurela, M., Timonen, H., and Hillamo, R.: High-Performance anion-exchange chromatography - mass spectrometry method for determination of levoglucosan, mannosan, and galactosan in atmospheric fine particulate matter, *Anal. Bioanal. Chem.*, 398, 2253–2264, 2010.

Schkolnik, G., Falkovich, A. H., Rudich, Y., Maenhaut, W., and Artaxo, P.: New Analytical Method for the Determination of Levoglucosan, Polyhydroxy Compounds, and 2-Methylerythritol and Its Application to Smoke and Rainwater Samples, *Environ. Sci. Technol.*, 39, 2744–2752, doi:10.1021/es048363c, 2005.

Schmidl, C., Marr, I. L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., and Puxbaum, H.: Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions, *Atmos. Environ.*, 42, 126–141, 2008.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, 33, 173–182, 1999.

Simoneit, B. R. T.: Biomass burning – a review of organic tracers for smoke from incomplete combustion, *Appl. Geochem.*, 17, 129–162, 2002.

Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P. M., Rogge, W. F., and Didyk, B. M.: Sugars Dominant Water-Soluble Organic Compounds in Soils and Characterization as Tracers in Atmospheric Particulate Matter, *Environ. Sci. Technol.*, 38, 5939–5949, doi:10.1021/es0403099, 2004.

Szidat, S., Jenk, T. M., Synal, H.-A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by  $^{14}\text{C}$ , *J. Geophys. Res.*, 111, D07206, doi:10.1029/2005jd006590, 2006.

Wan, E. C. H. and Yu, J. Z.: Determination of sugar compounds in atmospheric aerosols by liquid chromatography combined with positive electrospray ionization mass spectrometry, *J. Chromatogr. A*, 1107, 175–181, 2006.

## Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Yttri, K. E., Dye, C., Braathen, O.-A., Simpson, D., and Steinnes, E.: Carbonaceous aerosols in Norwegian urban areas, *Atmos. Chem. Phys.*, 9, 2007–2020, doi:10.5194/acp-9-2007-2009, 2009.

Zdráhal, Z., Oliveira, J., Vermeylen, R., Claeys, M., and Maenhaut, W.: Improved Method for Quantifying Levoglucosan and Related Monosaccharide Anhydrides in Atmospheric Aerosols and Application to Samples from Urban and Tropical Locations, *Environ. Sci. Technol.*, 36, 747–753, doi:10.1021/es015619v, 2002.

Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E. S.: Source Apportionment of PM<sub>2.5</sub> in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers, *Environ. Sci. Technol.*, 36, 2361–2371, doi:10.1021/es011275x, 2002.

AMTD

4, 4539–4560, 2011

---

**Levoglucosan and its isomers by LC-ESI-MS/MS**

---

C. Piot et al.

---

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Table 1.** Instrumental conditions.

Spray voltage (kV)	6.44
Spray current (µA)	4.46
Sheath gas flow rate	40.84
Auxillary gas flow rate	21.32
Sweep gas flow rate	12.03
Capillary temperature (°C)	310.07

## Title Page

## Abstract

## Introduction

## Conclusions

## Figures

14

1

Back

Close

Full Screen / Esc

[Printer-friendly Version](#)

## Interactive Discussion



## Levoglucosan and its isomers by LC-ESI-MS/MS

C. Piot et al.

**Table 2.** Analytical performances and linear regression parameters of levoglucosan (same performances for mannosan and galactosan).

	LC-MS	GC-MS
LOD <sup>a</sup> ( $\mu\text{g l}^{-1}$ )	30	100
Masse LOD ( $\mu\text{g}$ )	0.06	0.1
LOQ <sup>b</sup> ( $\mu\text{g l}^{-1}$ )	100	333
Analytical concentration range ( $\mu\text{g l}^{-1}$ )	20–200	100–5.10 <sup>5</sup>
RSD for high concentration <sup>c</sup> (%)	10	3
RSD for low concentration <sup>c</sup> (%)	5	5
$R^2$	0.996	0.963

<sup>a</sup> 3 × standard deviation of the blank

<sup>b</sup> 10 × standard deviation of the blank

<sup>c</sup> successively 5 injections of standard solution.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

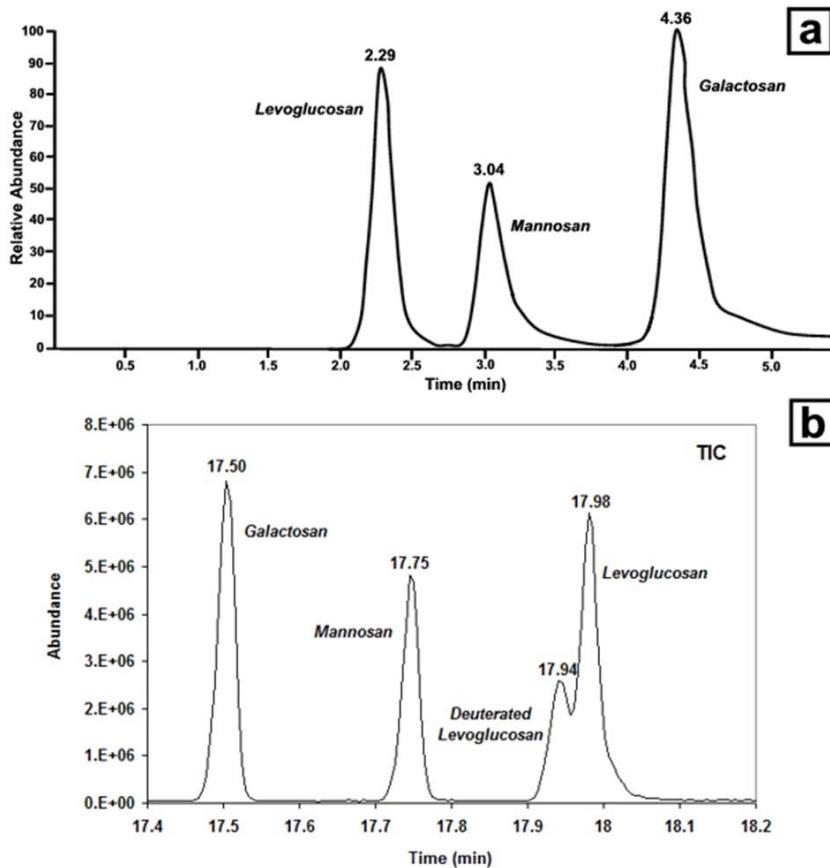
[Printer-friendly Version](#)

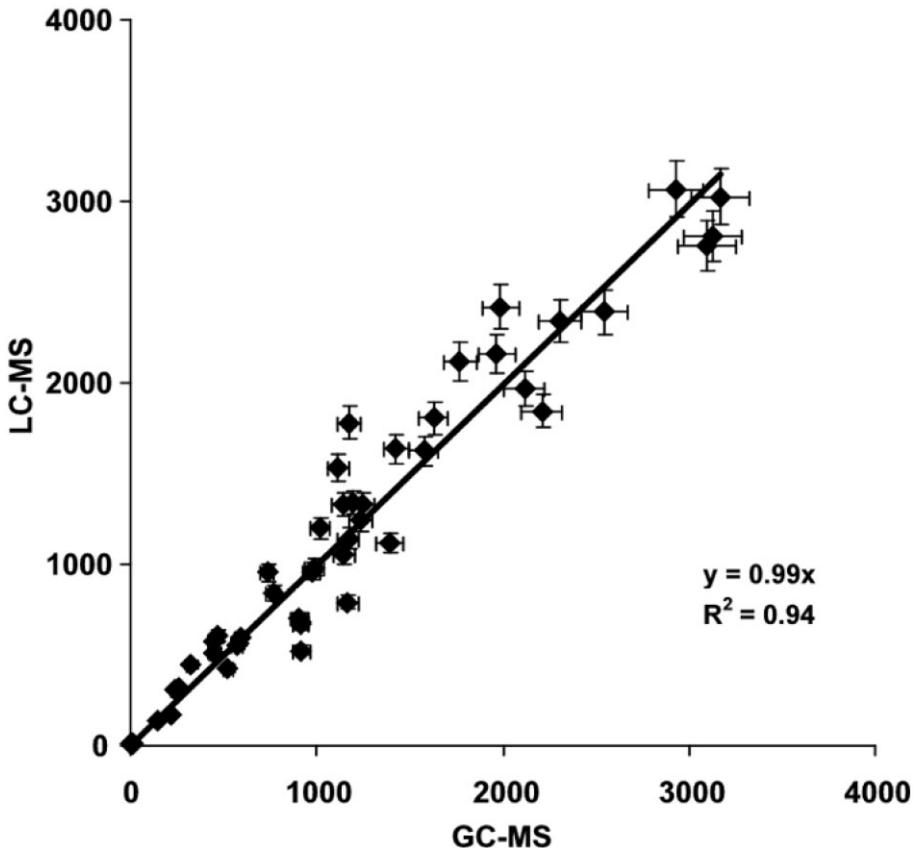
[Interactive Discussion](#)



**Levoglucosan and its isomers by LC-ESI-MS/MS**

C. Piot et al.

**Fig. 1.** LC-MS chromatogram (a) and GC-MS chromatogram on total ion current (TIC) (b).



**Fig. 2.** Correlation between LC-MS results and GC-MS results for levoglucosan (50 samples analysed). Concentrations are in  $\text{ng m}^{-3}$  in air. Error bars represent the RSD.