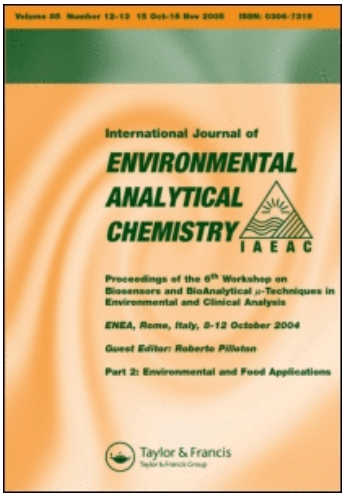

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A simplified method for levoglucosan quantification in wintertime atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection

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A simplified method for levoglucosan quantification in wintertime atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection

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Levoglucosan, a tracer for the assessment of the biomass burning contribution to atmospheric particulate matter (PM) concentrations, was determined by means of high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD). In this work we propose a modification in the instrumental set-up aiming at an improvement in the detector response by adding NaOH after chromatographic separation to increase the pH. The comparison between this technique and the gas chromatography/mass spectrometry (GC/MS) method commonly used showed good agreement. Repeatability is 4.8% RSD, limits of detection for pevoglucosan, mannosan and galactosan are in the range 0.001–0.002 $\mu g\,mL^{-1}$ in solution, corresponding to 3–4 $ng\,m^{-3}$ for 24 m^3 of air sampled. PM10 samples were characterised for levoglucosan and for organic and elemental carbon contents. The preliminary results reported here for five sites in the Lombardy region (Northern Italy) are, as far as we know, the first data on levoglucosan contribution to OC in Italy. The levoglucosan concentrations observed in Lombardy vary in the range 173–963 $ng\,m^{-3}$ with an average levoglucosan-C to OC ratio ranging from 1.5% to 2.5%.

Keywords: atmospheric aerosol; levoglucosan; HPAEC-PAD; anhydrosugars; biomass burning

1. Introduction

Many studies have recently focused on the determination of elements and organic compounds, which can serve as markers for specific sources of atmospheric particulate matter (PM). This is the case for saccharides, such as levoglucosan (1,6-anhydro-β-D-glucopyranose). This compound is an anhydrosugar, which is considered together with soluble potassium, as a good signature of biomass/wood combustion in atmospheric particulate matter samples [1,2]. It is noteworthy that potassium can also originate from soil and other sources such as meat cooking, waste incinerators and coal usage [3–7]. Therefore, levoglucosan can be regarded as a more specific tracer for biomass/wood burning [8].

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Wood smoke contains high concentrations of levoglucosan as it is a degradation product and arises from the pyrolysis of cellulose [1]. It is one of the most abundant organic components of smoke particles and is emitted during biomass burning processes together with compounds present in minor quantities such as terpenoids, resins, gums and biopolymers. Minor quantities of levoglucosan isomers, i.e. galactosan and mannosan, are emitted too. These two stereoisomers result from the pyrolysis of hemicellulose and are also specific markers for biomass burning. It is interesting to note that the mannosan to levoglucosan ratio allows the estimation of the proportion between hard- and softwood smoke in atmospheric PM [8]. Recently [9], mannosan and galactosan have been suggested as specific tracers for combustion of contemporary biomass with levoglucosan in regions where a significant use of brown coal containing fossilised cellulose can be observed.

In contrast to other molecular markers of biomass burning (e.g. diterpenoids, triterpenones) levoglucosan is emitted in large amounts, is sufficiently stable, is specific to cellulose-containing combustible and meets all important criteria to serve as an ideal molecular marker of biomass burning [10].

In the last years, increasing efforts have been devoted to levoglucosan quantification and the analytical methods most widely employed for this purpose have been reviewed [11]. They can be divided into two main categories: gas chromatographic (GC) techniques and methods based on liquid chromatography (LC) analysis.

Up to now, GC/MS has been the most commonly applied technique for levoglucosan quantification [10,12–14]. Even if the procedure for GC/MS analysis is well established, the main drawback is that it requires extraction with organic solvents, evaporation, and a final step of derivatisation to trimethylsilyl ethers.

Although GC/MS allows the determination of numerous species in a single analysis with a good resolution, it is time consuming and expensive because of the sample preparation step. For LC analyses different systems can be used as widely described in the literature [15–20]. In particular, a methodology recently suggested in the literature [21–25] is based on High Performance Anion Exchange Chromatography (HPAEC) coupled with Pulsed Amperometric Detection (PAD). Anion-exchange chromatography is generally applied to the analysis of carbohydrates in samples of different nature [26].

In our study, levoglucosan has been quantified by both GC/MS and HPAEC coupled with PAD. HPAEC-PAD is sensitive, precise, and accurate and does not require any complex extraction procedure followed by derivatisation in contrast to GC/MS analyses. Indeed, the sample preparation is very simple and levoglucosan can be directly analysed in aqueous extracts, which are also used for the determination of the PM ionic content. Nevertheless, it should be taken into account that the HPAEC-PAD technique is hindered by an interference problem between levoglucosan, and arabitol, a polyol. However, the interference problem was overcome first by Caseiro *et al*. [22] and further by Iinuma *et al*. [25].

In comparison with previous works [21–23], the method proposed here for HPAEC-PAD analyses in PM samples has been optimised adding concentrated NaOH post-column in order to improve the detector response. Moreover, in order to be able to use an instrument operating in the isocratic mode it was equipped with a system for regenerating the analytical column. A novel approach to solve the interference between levoglucosan and arabitol (applied here on wintertime samples) will be also shown.

Wintertime particulate matter samples were analysed for levoglucosan, and for organic (OC) and elemental (EC) carbon. OC and EC were measured by a Thermal Optical Transmittance method (TOT). It is noteworthy that if the levoglucosan/OC ratio for wood

emissions due to wood stoves or fireplaces is known, levoglucosan measurements allow the estimation of the primary contribution of these sources to ambient particulate matter [5,27,28].

In the literature many data have been recently published on levoglucosan concentrations at different sites in Europe [29] but similar data at Italian sites are still very scarce [13,30].

In the frame of a study aiming at the assessment of the residential wood combustion source, which has not a negligible contribution to particulate matter concentrations according to regional and national emission inventories [31], PM samples collected at different locations in the Lombardy region (Northern Italy) have been analysed for levoglucosan, OC and EC. The sampling sites have been chosen according to the possible different contributions for wood combustion to particulate matter emissions.

The preliminary data reported here are, as far as we know, the first data on the levoglucosan contribution to OC at Italian sites and among the few studies [13] on levoglucosan concentrations in PM10 samples in Italy. In order to assess the impact of wood smoke on PM emissions, a more detailed and extensive study is in progress. In particular, the quantification of biomass burning sources will be achieved taking into account the chemical profiles from wood smoke samples derived by the combustion of different kinds of wood burnt in stoves or in fireplaces.

2. Experimental

2.1 *Chemical*

To extract the samples and prepare the standard solutions 18.2 $M\Omega\,cm^{-1}$ water (MQ-water, Millipore) was used. Standards of levoglucosan (316555, CAS 498-07-7), mannosan, and galactosan were purchased from Sigma-Aldrich.

For the mobile phase, diluted sodium hydroxide solutions were prepared from 50% (w/w) NaOH (Fluka 72064).

2.2 *Instrumentation*

The analyses were carried out by means of an ion chromatograph (Dionex ICS1000) equipped with an isocratic pump and a sample injection valve with a 100 μL sample loop. The Chromeleon software was employed for the system control and data analysis. Different anhydrosugars (levoglucosan, mannosan, and galactosan) were separated using a Carbopac PA-10 guard column (50 mm × 4 mm) and a Carbopac PA-10 anion-exchange analytical column (250 mm × 4 mm). As eluent, NaOH 18 mM was used. Each analysis took 25 min and was followed by the regeneration of the analytical column consisting in rinsing the column with a more concentrated eluent (NaOH 200 mM); to this aim, the original two-way eluent flow valve was replaced by a three-way valve (see Figure 1, box a). The column was regenerated for 25 min at the end of each analysis in order to obtain reproducible retention times, to elute compounds retained in the column, and finally to preserve the column from carbonate formation. Moreover, to improve the reproducibility the column was re-equilibrated for a period of 15 minutes before starting a new measurement. The Chromeleon software allowed the valve position to be directly controlled. Two eluent tanks, connected to the eluent flow valve, were filled with NaOH 18 mM and 200 mM, respectively. To prevent CO_2 absorption and consequent carbonate

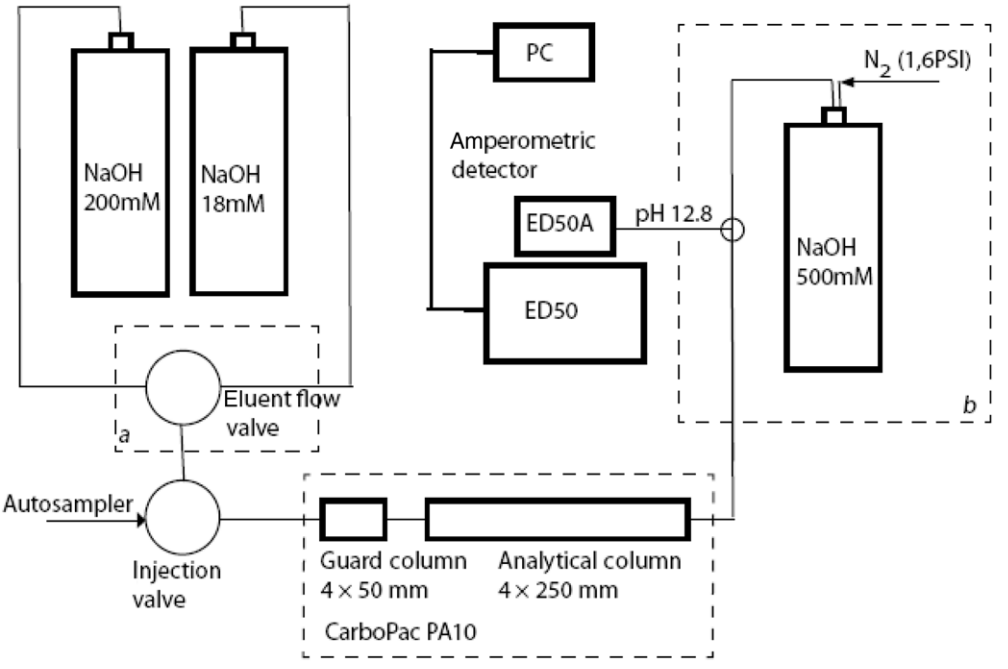

Figure 1. Instrument scheme: three-way valve for column regeneration (box a) and NaOH post-column addition (box b).

Table 1. Eluent program and set-up of flow valve.

Time	Eluent flow valve	Eluent	Acquisition	
0	OFF	NaOH – 18 mM	OFF	Re-equilibration
15	OFF	NaOH – 18 mM	ON	Injection
40	ON	NaOH – 200 mM	OFF	Regeneration
50				End

contamination of the eluent, both tanks were purged by a low He flow. The analysis program is schematically reported in Table 1.

The LC system comprised an amperometric detector (Dionex ED50) equipped with an electrochemical cell. The detector cell had a disposable gold electrode and a pH electrode as reference (both from Dionex) and was operated in the Pulsed Amperometric Detection (PAD) mode.

In this work, detector sensitivity to different potential cycles was examined: two pulse patterns, defined as waveform A and waveform B (Table 2) were tested. Waveform A uses a measuring potential of 0.10 V and waveform B 0.22 V. The first one is generally suggested for carbohydrates analysis while the second one is for amino-acids determination. Our measurements were carried out using waveform B (see Section 3.2).

In order to improve the analytical response (see the Results and discussion section), the pH of the solution was increased by post-column addition of NaOH 500 mM as shown in Figure 1 (box b).

Table 2. Amperometric detector pulse patterns for sugars.

Time (s)	Potential (V)	Function
Waveform A (Dionex Tech Note 21)		
0–0.2	+0.10	Delay
0.2–0.4	+0.10	Integration
0.41–0.43	−2.00	Cleaning
0.43–0.44	+0.60	Conditioning
0.44–0.50	−0.10	Conditioning
Waveform B		
0–0.04	−0.20	Conditioning
0.05–0.21	+0.00	Delay
0.21–0.22	+0.00	Integration begin
0.22–0.46	+0.22	
0.46–0.56	+0.00	Integration end
0.57–0.58	−2.00	Cleaning
0.58–0.59	+0.60	Conditioning
0.59–0.60	−0.20	Conditioning

2.3 *GC/MS analysis*

Levoglucosan concentrations were also determined on selected samples by means of GC/MS using a quadrupole instrument (Agilent Technologies 5973). The sample preparation, the quantification procedure, and the GC/MS analytical conditions are those reported in Pashynska *et al.* [10]. Methyl-β-L arabinopyranoside was used as internal recovery standard for levoglucosan [32]. Briefly, a portion of 1.5 cm^2 of quartz filter (12 samples in total) was spiked with methyl-β-L arabinopyranoside (6 μg), and extracted for 30 min with 20 mL of dichloromethane-methanol (80 : 20, v/v) under ultrasonic agitation. The extract volume was reduced with a rotary evaporator to about 1 mL. The extract residue was trimethylsilylated with MSTFA + 1% TMCS and pyridine (2 : 1, v/v) and the reaction was carried out for 60 min at 70°C. One μL of the derivatised solution was immediately analysed by GC/MS. The levoglucosan recovery percentage was 101.7% ± 5.1% for GC/MS.

2.4 *Sample collection*

PM10 (particulate matter with aerodynamic diameter smaller than 10 μm) was sampled using low-volume samplers operating at 1 $m^3 h^{-1}$. Twenty-four-hour samples were collected on quartz fibre filters (diameter 47 mm, sampled area 12 cm^2), which were pre-fired at 700°C for 1 h. This pre-firing procedure was chosen after having checked three different baking protocols [33].

PM10 was sampled by the Environmental Protection Agency at five sites in Lombardy (Northern Italy) during the period 21–27 February 2005. The sampling sites have different geographical characteristics as reported in Figure 2.

The PM mass concentration was determined using an analytical microbalance (sensitivity 1 μg) after 48 hours conditioning at humidity and temperature controlled (35% ± 5%, 20°C ± 2°C) according to the protocol adopted by the Environmental

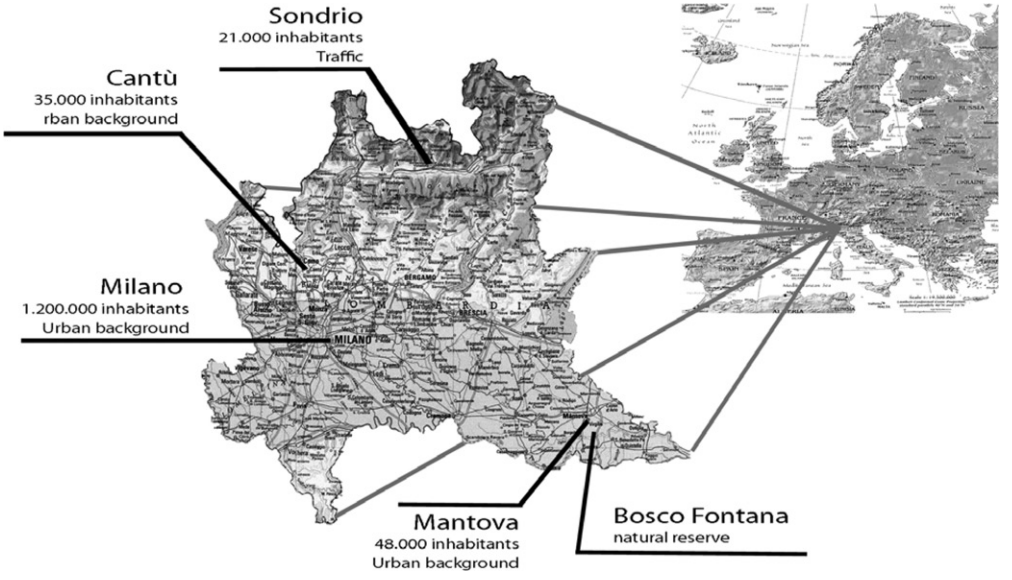

Figure 2. Map of sampling sites in Lombardy (Northern Italy).

Protection Agency of Lombardy. The uncertainty on mass concentration measurements was $\pm 2\,\mu g\ m^{-3}$ and the detection limit was $2\,\mu g\ m^{-3}$.

2.5 *Sample extraction and recovery*

The HPAEC-PAD analytical procedure was optimised to analyse levoglucosan and its isomers in particulate matter samples using the same solutions already prepared for the inorganic ions quantification. This procedure is less time consuming than GC/MS and the sample can be stored for further analyses.

In this work, one punch ($1.5\,cm^2$) cut from a quartz fibre filter was analysed after extraction with 6 mL MQ-water in an ultra-sonic bath [34]. Undissolved sample material and filter debris were removed from the sample solution by filtration (5 μm filter, by Dionex) before injection.

The sample preparation consists of three subsequent extractions in an ultra-sonic bath for 20 min with the renewal of the solution in contact with the filter at each step. All samples were analysed immediately after extraction or during the subsequent 24 hours. To verify that the extraction procedure was also suitable for levoglucosan, test samples were prepared using 12 punches (area $1.5\,cm^2$) taken from pre-fired quartz fibre filters. They were spiked with 20 μL of 250 ppm levoglucosan solution ($5\,\mu g\ sample^{-1}$) and dried for 24 hours. The levoglucosan recovery percentage was $98.7\% \pm 7.0\%$ for HPAEC-PAD.

In contrast to the sample preparation for GC/MS analysis, the HPAEC-PAD analytical approach does not involve extraction with organic solvents, reduction of the solvent volume and derivatisation. Moreover, the simpler extraction procedure does not need the use of an internal standard for recovery calculation as done in GC/MS. All these features make the method cheaper and less time consuming than GC/MS.

3. Results and discussion

3.1 *Response increase with pH*

The instrumental response factor (C min g^{-1}) was calculated as the ratio between the peak area (C min) and the quantity of the injected analyte (g). It is worth noting that in order to achieve a good separation of the analytes, the eluent concentration should not be too high (i.e. high pH values). At the same time, it is well known that the detector sensitivity for carbohydrates is lower at lower pH [22] while an improvement can be observed increasing NaOH concentration. In particular, for the separation and quantification of the less retained analytes (such as levoglucosan) the need of high sensitivity can compete with technique selectivity.

To overcome these problems, we introduced an improvement consisting in the post-column addition of the eluent at higher concentration (NaOH 500 mM), which produced an increase in the pH of the solution and a consequent enhancement of the instrumental response. In particular, varying the pressure in the tank with the post-column eluent, we were able to add different quantities of NaOH 500 mM in the eluent flow by means of a T-joint (see Figure 1, box b). The detector measured the pH of the solution using the reference electrode. The pattern of the response factor as a function of pH is reported in Figure 3, where the highest sensitivity occurred at pH = 12.7. This pH value was obtained adding 0.1 mL min^{-1} of the NaOH (500 mM) solution to the eluent coming from the column; in our experimental set-up this corresponded applying a counter pressure of 1.6 PSI.

3.2 *Instrumental response with different waveforms and chromatographic separation*

As mentioned before, we obtained a good separation of the anhydrosugars by means of an isocratic pump, cleaning the column from the possible presence of non-eluted species introducing a more concentrated NaOH solution by means of a three-way valve (see the Instrumentation section). In other literature studies [23–25], a gradient system was typically used.

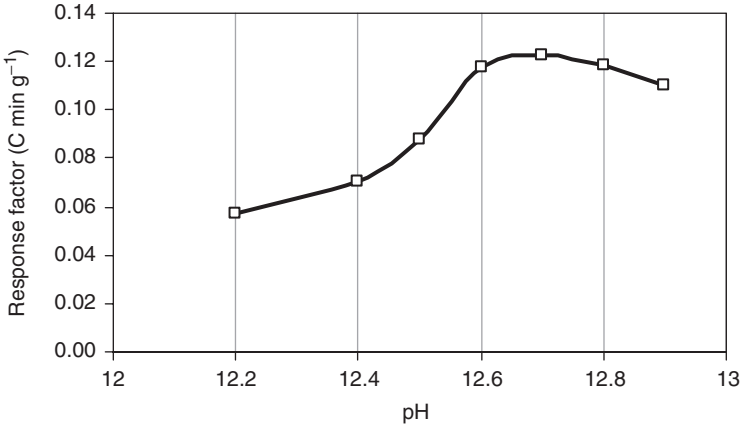

Figure 3. Response factor (C min g^{-1}) as a function of pH.

Table 3. Response factor for levoglucosan, mannosan, and galactosan (C min g^{-1}).

	Levoglucosan	Mannosan	Galactosan
Waveform A	0.10	0.11	0.11
Waveform B	0.16	0.19	0.18

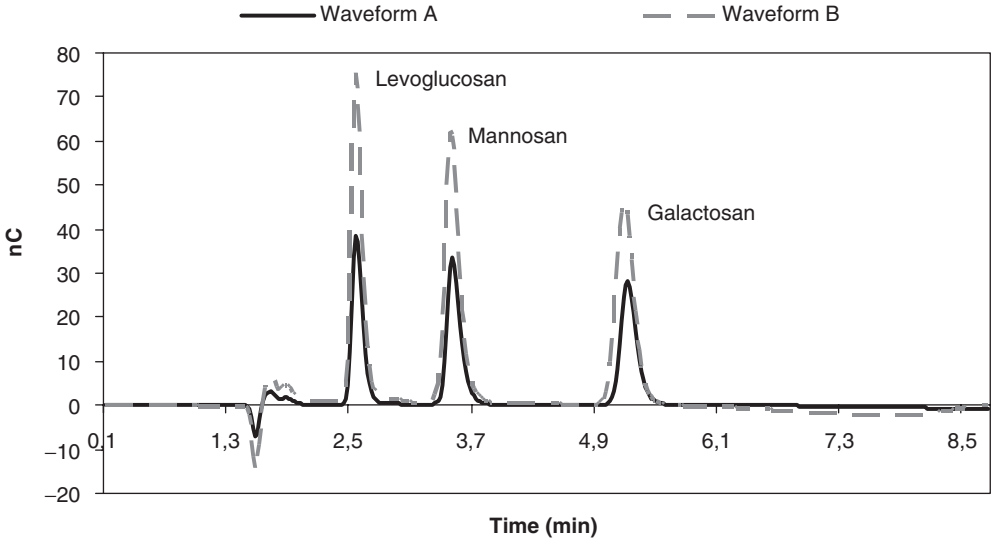

Figure 4. Chromatograms of the standard solution registered with two different potential cycles.

The instrumental performances were checked analysing standard solutions at different concentrations containing the three anhydrosugars (levoglucosan, mannosan and galactosan) and glucose. We decided to add glucose to the standard solution to verify the correct performance of the instrument comparing the experimental response with the expected one according to manufacturer's specifications [35]. Indeed, a test on retention time stability can be carried out with glucose because it is more retained than anhydrosugars. In our conditions the detector calibration and the separation performance was observed to be stable for 1 week.

In Table 3 the variation of the analytes response with the two different applied potentials is shown. The comparison shows a significant increase in the instrumental response for the three anhydrosugars using waveform B. Consequently, waveform B was chosen for the analyses. Chromatograms of the standard solution registered during the two different potential cycles are reported in Figure 4. It is noteworthy that waveform B is suggested by the constructor for amino-acids analyses, as they are not detected when waveform A is applied. However, we used waveform B for anhydrosugars measurements as it showed a better response. Moreover, aminoacids are not a probable analytical interference since they are not retained at the above reported pH used for chromatographic separation [36]. Some PM10 samples ($n = 18$) have been selected in the concentration range (approximately 100–1000 ng m^{-3}) of interest to test our technique,

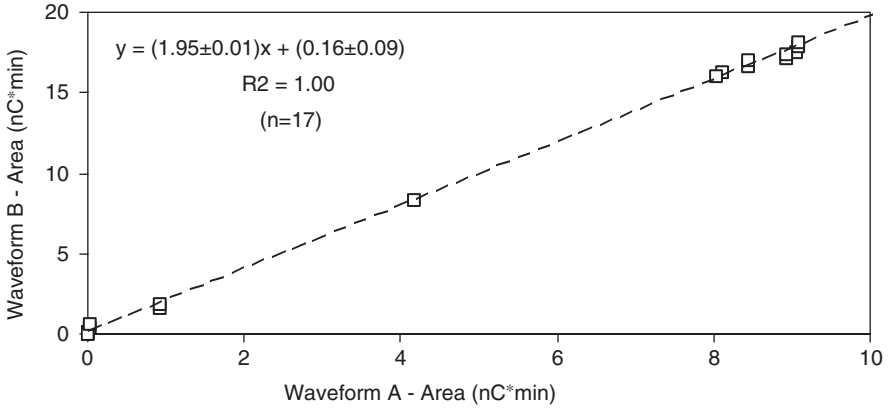

Figure 5. Comparison between the signals obtained using waveform A and waveform B for levoglucosan in a set of real PM samples.

Table 4. Analytical performance for three anhydrosugars with two different amperometric patterns.

	Levoglucosan	Mannosan	Galactosan
Waveform A			
Slope	9.38	10.84	11.00
Slope standard error	0.11	0.02	0.05
R^2	1.00	1.00	1.00
Number of standards	8	8	8
Waveform B			
Slope	15.93	18.77	18.01
Slope standard error	0.01	0.00	0.01
R^2	1.00	1.00	1.00
Number of standards	8	8	8

and have been analysed using the two different potential cycles. The comparison between the levoglucosan analytical signals obtained with waveforms A and B is reported in Figure 5. The very good correlation ($R^2 = 1$) highlights that possible interfering analyte concentrations are low when compared to levoglucosan and the slope (1.95) shows the sensitivity increase when using waveform B.

The technique is linear in the 0.010 ppm–2 ppm concentration range and the calibration parameters obtained for the three anhydrosugars are reported in Table 4.

3.3 *Analytical interferences*

As already mentioned, there is an interference problem between levoglucosan and arabitol with the HPAEC-PAD technique. Indeed, a partial overlapping for levoglucosan and arabitol peaks using a CarboPac PA10 analytical column and NaOH 0.5 mM as eluent can be observed. Moreover, other compounds (e.g. mannosan and mannitol) have the same retention time on the PA10 column as singled out in recent works [22,25]. Arabitol is

a polyol recently proposed as a tracer for the quantification of the contribution of fungal spores to PM [37]. Literature data on arabitol and levoglucosan atmospheric concentrations [8,17] show that during wintertime, the atmospheric concentrations of arabitol are much lower (about a factor 10–20) than those of levoglucosan so that intereference due to arabitol can be neglected in winter samples (as was done in our case). On the contrary, during summer and autumn when biological source emissions are more important, the arabitol interference must be taken into account.

Quantification of levoglucosan and arabitol in the literature was achieved by deconvolution of the unresolved chromatographic peaks. With the analytical procedure proposed in our study, the two species completely overlap and the interference cannot be eliminated by peak deconvolution. Consequently, an alternative method based on the hydrolysis of levoglucosan to glucose has been proposed to assess the presence of arabitol in real PM10 samples [17]. To completely hydrolyse levoglucosan to glucose a mixture of levoglucosan and arabitol has been treated with 0.1 M HCl at 85°C for 28 h. The standard solution with arabitol tested by hydrolysis was stable in these conditions. Two analyses are required for each sample in order to evaluate levoglucosan and arabitol contributions: the first one without hydrolysis and the second one after the hydrolysis. The peak observed after hydrolysis at the same retention time of levoglucosan is due to arabitol. This method was applied on seven PM10 samples suitably collected during wintertime 2006; as expected, results showed that after hydrolysis the peak corresponding to arabitol was not present. Unfortunately, we have no data on similar tests performed on summertime samples, as work is still in progress.

3.4 *Repeatability and limits of detection*

To test instrumental repeatability, three standards of levoglucosan solutions (in the 0.1–2 ppm range) were analysed five times with HPAEC-PAD and nine times with GC/MS. The repeatability (defined as the percentage relative standard deviation) for HPAEC-PAD, was 4.8% and for GC/MS, 5.5%.

The limits of detection (LODs) were calculated as the analyte concentration giving a signal equal to the blank signal, y_B, plus three standard deviations of the blank, s_B [38]. In our case, no contaminants were detected and the LOD was evaluated on extracts from blank filters.

In Table 5, LODs for levoglucosan, mannosan and galactosan are reported. They were obtained applying waveform B to the detector and setting the eluent at pH = 12.7. When we refer to 24-hour particulate matter samples, obtained by low volume samplers ($1\,m^3\,h^{-1}$) the LODs are reported as $\mu g\,m^{-3}$. These LODs are similar to those obtained by Caseiro *et al.* [22], but we used a smaller filter portion ($1.5\,cm^2$ vs. $4.5\,cm^2$). Thus, our

Table 5. Levoglucosan, mannosan and galactosan detection limits.

	Levoglucosan	Mannosan	Galactosan
LOD ($\mu g\,mL^{-1}$)	0.0018	0.0013	0.0015
LOD ($\mu g\,m^{-3}$)[a]	0.0036	0.0026	0.0030

Notes: [a]sampling flow rate = $1\,m^3\,h^{-1}$; sampling time = 24 h.

methodology is particularly useful when different analyses have to be carried out on the same filter.

3.5 *Comparison between HPAEC-PAD and GC/MS*

Anhydrosugar mass concentrations obtained by HPAEC-PAD and GC/MS techniques in selected wintertime particulate matter samples were compared. It is worth noting that the two methods differ significantly in separation and detection principles, and they use different sample preparation procedures. Nevertheless, a good agreement in levoglucosan concentrations was achieved as shown in Figure 6 ($R^2 = 0.97$). The good agreement between the two techniques suggests that arabitol, if present in real wintertime samples, did not significantly affect our measurements.

4. Application to PM10 samples

In PM10 samples collected at five different sites in Lombardy (Figure 2), organic carbon (OC) and elemental carbon (EC) were also measured. The OC/EC analyses were carried out by means of a Thermal-Optical Transmittance (TOT) analyser [39,40].

PM10 average mass concentrations during the sampling period ranged between 47.4 $\mu g\,m^{-3}$ registered in Sondrio, the alpine town, up to 100.2 $\mu g\,m^{-3}$ in Mantova, the town at the southern border of the Lombardy region.

Average OC concentrations were in the range 10.6–14.3 $\mu g\,m^{-3}$ with the highest value registered in Mantova and the lowest in Sondrio. The lowest EC average value (1.5 $\mu g\,m^{-3}$) was detected, as expected, at the monitoring site in the national reserve; this value must be compared with a concentration of 2.3–2.8 $\mu g\,m^{-3}$ measured at other sites (urban background) but in Sondrio, which is a traffic site (3.8 $\mu g\,m^{-3}$ as EC average concentration).

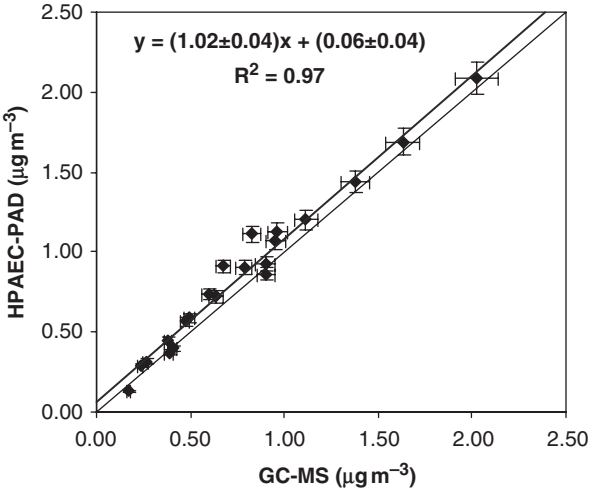

Figure 6. Correlation between HPAEC-PAD and GC/MS results (in $\mu g\,m^{-3}$) for levoglucosan.

The highest average levoglucosan concentrations were registered in Sondrio ($885\,ng\,m^{-3}$) and Cantù ($963\,ng\,m^{-3}$). These results are in agreement with information given by a survey carried out by the regional administration (PARFIL project), which identifies Sondrio as the city with the highest per capita wood use for domestic heating in Lombardy. The high levoglucosan concentrations measured at Cantù are ascribed to the industrial activities related to wood furniture production. The strong impact of wood combustion in these sites is also pointed out by the average levoglucosan-C to OC ratio, which is 2.5% in Sondrio and 2.1% Cantù to be compared to approximately 1.6% in Milan, Mantova, and Bosco Fontana. In Milan, the low levoglucosan average concentration ($385\,ng\,m^{-3}$) and the levoglucosan-C/OC ratio (1.6%) highlight the importance of other sources (i.e. traffic or industries) contributing to OC at this urban site. The values registered in Lombardy are similar to those found at other sites in Europe [10,25,28].

Relatively low levoglucosan concentrations were also registered at Bosco Fontana (the monitoring station located in the natural reserve) and the levoglucosan-C/OC ratio (1.5%) was quite similar to the one registered in Milan (1.6%) or Mantova (1.6%), suggesting that Bosco Fontana was not strongly affected by wood burning. In Mantova, the levoglucosan average concentration is higher than in Bosco Fontana ($569\,ng\,m^{-3}$ versus $405\,ng\,m^{-3}$) indicating that residential wood combustion is larger in the urban area, where stoves and fireplaces are more abundant. This result mirrors recent findings for three Austrian regions [5]. Moreover, levoglucosan data in Mantova show a stronger variability than in the natural reserve, where less modulated levels suggest the presence of a background concentration.

5. Conclusions

In this paper, we have shown that with a simple approach using an instrument operating in the isocratic mode levoglucosan, mannosan, and galactosan determination is possible, and that a post-column treatment improves analytical stability and sensitivity. In addition, the choice of waveform B increases the sensitivity. The method here presented was tested against the GC/MS method with successful results. It is noteworthy that HPAEC-PAD is cheaper, and less time- and labour-intensive than gas chromatographic procedures.

A drawback of this technique is the co-elution of levoglucosan and arabitol, which needs a hydrolysis procedure in the case of summertime samples. Indeed, this interference problem for ambient particulate matter samples is more important in summer and autumn than in winter. The method proposed here is well suited for determining levoglucosan and its isomers in emission samples by biomass smoke and wintertime ambient PM samples. Preliminary results obtained examining samples from different sites in the Lombardy region, highlight that alpine cities (such as Sondrio), during wintertime are more influenced by wood smoke than the rest of the region. High levoglucosan concentrations measured at all sites point out that wood burning is an important regional primary PM source.

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