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Direct Determination of Levoglucosan at the Picogram per Milliliter Level in Antarctic Ice by High-Performance Liquid Chromatography/ Electrospray Ionization Triple Quadrupole Mass Spectrometry

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A method for the direct determination of levoglucosan at the picogram per milliliter level in less than 1 mL of Antarctic ice has been developed. Chemical analysis is performed by high-performance liquid chromatography with triple quadrupole tandem mass spectrometric detection. Levoglucosan, a specific molecular marker for biomass burning, is identified by negative ion electrospray mass spectrometry using *m/z* 161/113, 161/101, 161/85, and 161/71 as monitoring ion transitions. Contamination problems were carefully taken into account by adopting ultraclean procedures during sampling and sample pretreatment phases. The limit of detection is 3 pg mL^{-1} (0.3 pg absolute amount injected); the repeatability ranges between 20% and 50% at a concentration of 20 and 9 pg mL^{-1}, respectively. This methodology allowed the direct determination of levoglucosan in a 1 mL sample of Antarctic ice with concentration ranges between 4 and 30 pg mL^{-1}. To our knowledge these are the first levoglucosan concentrations reported for Antarctic ice.

Biomass burning is a significant source of aerosol particles to the atmosphere which produces an impact on global climate by absorbing radiation but also by acting as cloud condensation nuclei,[1] often affecting regional and local air quality. In the past few decades it has become evident that the atmospheric aerosol is an important pathway by which trace elements and organic compounds are transported both locally and on a remote scale given that aerosol particles can persist in the troposphere for days to weeks, depending on their sizes and chemical compositions.

The chemical composition inventory of aerosol particulate matter is important for understanding the organic component contribution of biomass burning emissions to atmospheric chemistry and complements existing data on the signatures of direct organic emissions from biomass sources.[2] The pyrolysis derivatives from the thermal breakdown of cellulose during burning events are the dominant smoke tracers in continental airsheds.[3] Important compounds from biomass burning are the monosaccharide anhydrides (MAs), and the most important tracer compound among them is levoglucosan (1,6-anhydro-β-D-glucopyranose) with lesser amounts of galactosan (1,6-anhydro-β-D-galactopyranose) and mannosan (1,6-anhydro-β-D-mannopyranose).[4] These are the specific molecular tracers utilized for the assessment of particulate matter composition from biomass burning in the atmosphere because they cannot be generated by noncombustive processes or by nonwood combustion. Molecular markers such as MAs are important tools in tracking the transport of particles produced by biomass burning. Among them, levoglucosan has been considered an excellent choice because it is emitted in large quantities and is stable in the atmosphere. There is evidence to suggest possible conversion of levoglucosan into organic acids,[5] but Fraser and Lakshmanan[6] tested the stability of levoglucosan subjected to acid-catalyzed hydrolysis under atmospheric conditions and found no degradation over 10 days.

Even though the MAs and in particular the levoglucosan content of organic aerosols have been the topic of many studies, a diversity is seen in the methodologies for the chemical analysis. Various chromatographic techniques have been used for MAs analysis including gas chromatography/mass spectrometry (GC/MS) after derivatization and high-performance liquid chromatography (HPLC) by various detectors[7−9] among which high-

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resolution mass spectrometry was included.[10] Schkolnik and Rudich,[11] in a review on detection and quantification in atmospheric aerosols, report that GC with a mass spectrometer as the detector is the most commonly used method for levoglucosan quantification despite requiring long preparation time and dry conditions. In the quality control of the analytical procedure they report for GC/MS an uncertainty range between 2% and 20% and a limit of detection (LOD) between 1×10^5 and 3.4×10^5 pg mL^{-1}. Recently alternative methods using HPLC with mass spectrometric detection have been proposed, and great efforts have been directed toward simple, fast, precise, accurate, and possibly direct analytical methods. Engling et al.[12] report a high-performance anion-exchange chromatography method with pulsed amperometric detection for the determination of anhydrosugars in smoke aerosol that requires minimal sample preparation. They estimated for levoglucosan analysis a precision of 5.3% and an analytical LOD of 2×10^3 pg mL^{-1}. Dixon and Baltzell[7] investigating HPLC with aerosol charge detection for the analysis of the main MAs in atmospheric aerosols reported for levoglucosan an LOD of 9×10^4 pg mL^{-1} that was lower than the lowest LODs listed by Garcia et al.[13] using electrophoretic microchip with pulsed amperometric detection CE-PAD (2.7×10^6 pg mL^{-1}) and by Schkolnik et al.[14] using ion-exclusion HPLC and spectroscopic detection (5×10^5 pg mL^{-1}) but higher than electrospray ionization ESI-MS [5] (6×10^4 pg mL^{-1}) and high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD)[12] (2×10^3 pg mL^{-1}).

In order to put in the right perspective the current concentrations of levoglucosan in the atmosphere, it is important to quantify the fluxes of this compound during the past, by examining environmental archives such as snow and ice cores. Polar ice core studies have extensively documented large changes in the content of aerosol constituents such as ionic species,[15] dust,[16,17] trace elements,[18,19] and organic compounds[20–22] during the late Quaternary period. In particular Legrand and De Angelis[22] confirm the use of ammonium formate and oxalate content to trace inputs from forest fires into Greenland ice. Ice cores benefit from three relevant advantages for studying atmospheric constituents over a long time scale. First, the properties of most of the aerosol compounds remain unaltered in a low-interference matrix such as ice, second, their deposition can be dated precisely, and finally, their flux can be calculated via the fairly well-known past accumulation rate. The chemical information stored in ice can be used to reconstruct the climate, the environment, and in this work, via the levoglucosan concentration, the biomass burning events on earth thousands of years before modern times.

The objective of this work was to develop an HPLC with triple quadrupole tandem mass spectrometry (HPLC/ESI-MS/MS) method for the determination of levoglucosan in less than 1 mL of Antarctic ice without the need of any kind of preconcentration. To our knowledge, this is the first time that a triple quadrupole tandem mass spectrometry method for direct determination of levoglucosan in polar ice samples has been reported.

EXPERIMENTAL SECTION

Reagents and Materials. At the Laboratory of Glaciology and Geophysics of the Environment (LGGE)[23] a mixed bed of ion-exchange resins (maximum flow rate was 2 L h^{-1}) from Maxy (La Garde, France)[24] was used to produce the ultrapure water used in the decontamination procedure. At the Department of Environmental Sciences (DES)[25] in Venice, the ultrapure water was produced by a Purelab Ultra system (Elga, High Wycombe, U.K.). Chloroform (Merck, Darmstadt, Germany) and Suprapur grade HNO_3 (65% Merck) were used in the initial phases of the labware washing method. Low-density polyethylene (LDPE) bottles used to contain the samples (from Nalgene Corporation, Rochester, NY) and the stainless steel tools for the decontamination of the ice cores were washed on a clean bench (class 100) located in a clean room (class 10000) at the LGGE.[24]

A levoglucosan standard used for external calibration with a purity of 99.7% was obtained from Sigma-Aldrich (Steinheim, Germany), galactosan and mannosan were from Molecula (Shaftesbury, U.K.), labeled levoglucosan ^{13}C6 98% isotopic enrichment, purity of 98%, was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA), ammonium hydroxide (25%) analytical grade was from Fluka (Buchs, Germany), and HPLC/MS grade methanol and water were from Romil Ltd. (Cambridge, U.K.).

The sample handling was done using Eppendorf pipettes and polyethylene tips (Hamburg, Germany), with polyethylene vials purchased from Agilent Technologies (Wilmington, DE).

Sample Collection and Processing. For this study an electromechanical drill was used to obtain the ice cores, which are cylindrical samples, with a diameter of about 10 cm, of the deep ice layers in the glaciers. The ice core sections were retrieved from Antarctica at Dome C (75°06′ S; 123°21′ E, 3233 m, mean annual temperature −54 °C) within the framework of the European Project for Ice Coring in Antarctica (EPICA).[17] Only a part

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of the cross section (about 30%) was available for this study, because in the EPICA program, a given core section (typically 55 cm long) is cut longitudinally into several parts which are then used for different kinds of determinations.

A drawback of deep electromechanical drilling is that ice cores are contaminated on their outside by several heavy metals and organic compounds originating from the wall retaining fluid, which is used in the field to avoid closure of the drilling borehole. The contamination of the samples, which may also derive from handling of the core, was carefully evaluated. Following this, a decontamination procedure, successfully adopted for many trace elements,[26–28] was performed by chiseling the external ice core layers under a class 100 laminar flow clean bench located in the cold laboratory ($t = -15$ °C) at the LGGE. The obtained uncontaminated inner core was cut into two parts and placed in two separate ultraclean 1 L LDPE bottles. The ice samples were then melted at room temperature under a class 100 clean bench, and an aliquot of about 5 mL was transferred to a 15 mL ultraclean LDPE bottle and kept frozen until analysis.

During the development of the method, the challenge was to obtain the lowest LOD through a careful control of contamination and a continuous check of the blanks. The risk of contamination necessitated the minimization of sample preparation; each phase of manipulation and preparation of the containers was carried out in a class 100 clean chemistry laboratory and a simple but strict protocol of cleaning was followed: at first every bottle or LDPE vial was washed in ultrapure water, cleaned in an ultrasonic bath three times in ultrapure water, carefully rinsed with ultrapure water, and stored in plastic bags until use, before use they were rinsed again with water. Melted ice was poured into a vial directly from the storage bottle and was directly analyzed after the introduction of a labeled levoglucosan internal standard. For this, 675 μL of melted ice was mixed with 25 μL of a 1.41×10^3 pg mL^{-1} levoglucosan ^{13}C in ultrapure water.

Instrumentation. Sample analysis was performed by using liquid chromatography/negative ion electrospray ionization–tandem mass spectrometry (HPLC/(−)ESI-MS/MS). An Agilent 1100 series HPLC system (Agilent, Waldbronn, Germany) with a binary pump, vacuum degasser, autosampler, and thermostatted column compartment was used.

For the chromatographic analysis, 100 μL of the sample was injected onto a C18 Synergy Hydro column (2.1 mm i.d. × 50 mm length, 4 μm particle size, Phenomenex, Torrance, CA), isocratic elution was employed, at 180 μL min^{-1} using a 15% v/v methanol solution in water. A 13 mM solution of ammonium hydroxide was added on-line after the chromatographic column using a model "11" syringe pump (Harvard Apparatus Inc., Holliston, MA) at a flow of 5 μL min^{-1}. The retention time of levoglucosan was at 1.5 min, and the run lasted 4 min.

An API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada) equipped with Turbo V source was used to determine levoglucosan in Antarctic ice. Data were collected in negative ion mode by multiple reaction monitoring (MRM) with a 200 ms dwell time/transition. In the MRM acquisition mode the first quadrupole (Q1) selected the parent ion while the third quadrupole (Q3) selected the fragment (daughter) ion of interest; both Q1 and Q3 were set at unit resolution (a peak width of 0.7 ± 0.1 amu at 50% of maximum peak height). Instrumental conditions are reported in Table 1.

Table 1. Instrumental Conditions and Measurement Parameters for API 4000

	ESI	APCI
curtain gas (psi)	35	35
nebulizer gas (psi)	45	40
auxiliary gas (psi)	50	20
source temperature (°C)	400	350
collision gas (psi)	6	8
ionization voltage (V)	−4500	
needle current (μA)		−3.5
orifice potential (V)	−54	−54
collisional focusing (V)	−4	−4

Table 2. Transition Monitored and Compound Parameter Collision Energy (CE) and Collision Cell Exit Potential (CXP) Settings for Levoglucosan and Labeled Levoglucosan

	Q1 m/z	Q3 m/z	CE (V)	CXP (V)
levoglucosan	161	113	−14	−20
	161	101	−14	−16
	161	87	−23	−15
	161	85	−23	−12
	161	71	−17	−7
	161	129	−13	−23
levoglucosan ^{13}C	167	118	−13	−19
	167	105	−14	−15
	167	89	−20	−14
	167	74	−19	−11

Collision energy (CE) (amount of energy that the precursor ions receive as they are accelerate into the collision cell) and collision cell exit potential (CXP) (a parameter which controls the collision cell exit potential used to focus and accelerate the ions after leaving the collision cell) are two important parameters, the first for ion fragmentation and the second for the ion transmission through the triple quadrupole. In order to achieve the highest possible sensitivity, CE and CXP were optimized by direct infusion of a 500 ng mL^{-1} solution of levoglucosan in ultrapure water into the ion source of the mass spectrometer. A summary of the transitions monitored and the compound parameters CE and CXP is given in Table 2.

The transitions 161/101 m/z for levoglucosan and 167/105 m/z for labeled levoglucosan were used for the quantification of sample.

RESULTS AND DISCUSSION

Instrumental Performance. After optimizing the mass spectrometer parameters (see above) by direct infusion of a levoglucosan solution in order to have the maximum instrumental sensitivity and analytical stability, the optimization of this method was performed by testing several commercially available HPLC columns and by varying the percentages of methanol and ammonia. Six commercially available HPLC C18 columns were tested for MAs selectivity and signal tailing: Luna NH_2 (100 mm × 2

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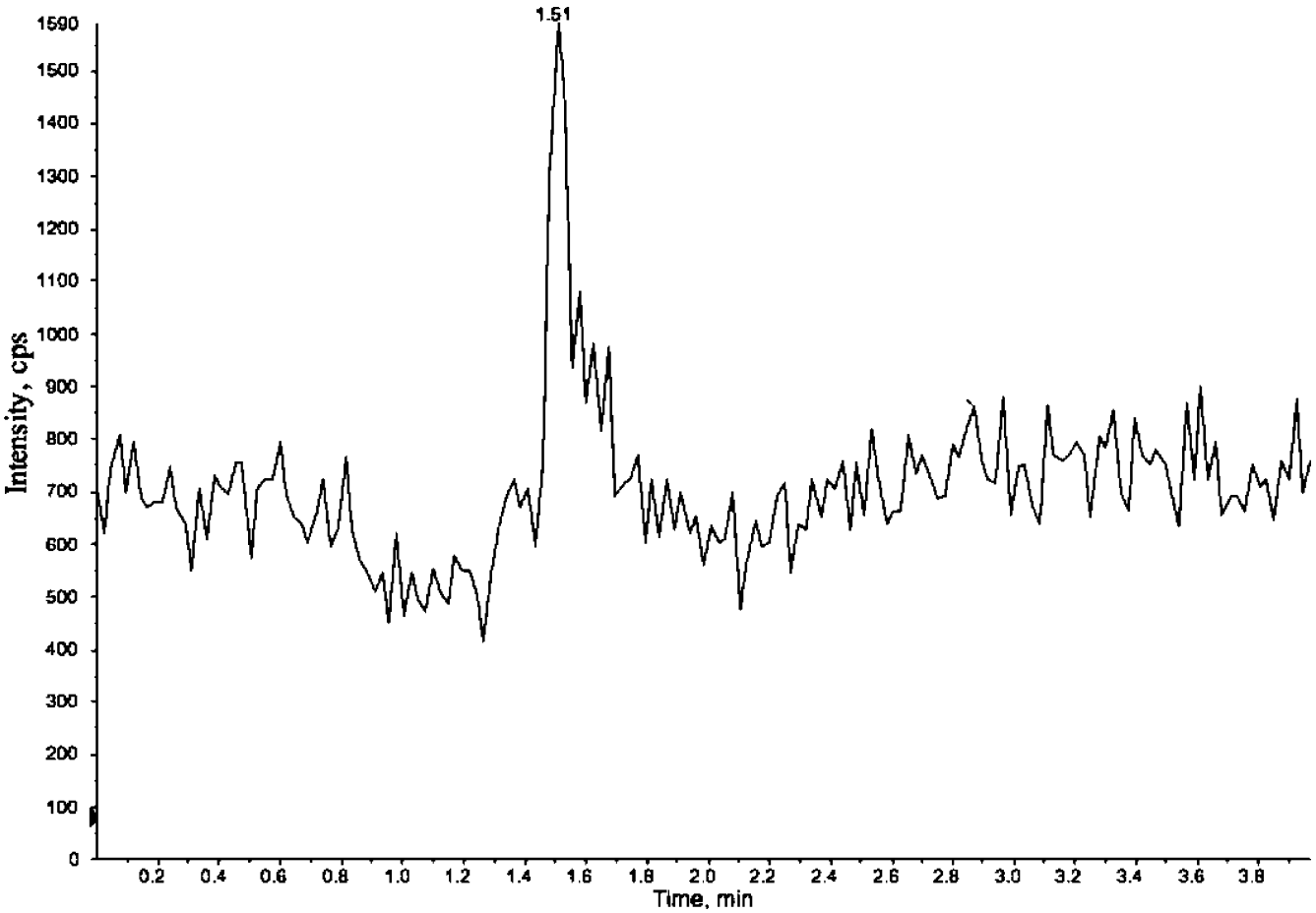

Figure 1. HPLC/ESI-MS/MS MRM chromatogram of levoglucosan in an Antarctic ice sample.

mm, 3 μm), Synergy Hydro (C18) (50 mm × 2.1 mm, 4 μm), both from Phenomenex, Zorbax SB C3 (100 mm × 3 mm, 3.5 μm), Zorbax Eclipse XDB (C18) (150 mm × 4.6 mm, 5 μm), Zorbax SB CN (250 mm × 4.6 mm, 5 μm), and Zorbax SB Aq (150 mm × 2.1 mm, 3.5 μm), all from Agilent Technologies; although the column-generated background noise was low, none of these columns showed a high selectivity for the MAs. Due to the extremely low concentration of the MAs in ice samples, and the difficulty in separating the three target stereoisomers, we chose to focus our attention on increasing the instrumental sensitivity to the detriment of the chromatographic separation of the MAs. In this respect, we have chosen as the stationary phase the Synergy Hydro column that gave the narrowest peak width and greatest peak height for the three MAs.

Regarding the atmospheric abundance of MAs, Simoneit et al.[2,3] reported that levoglucosan, galactosan, and mannosan are produced during biomass burning from combustion of cellulose and hemicellulose, but levoglucosan is produced in much larger quantities (about >90% in vegetation smoke). Levoglucosan was found to be the major organic compound in atmospheric particulate matter in urban areas impacted by wood smoke.[3] Jordan et al.[29] found that levoglucosan was the major constituent of smoke from biomass burning in ambient air samples collected in Launceston, Australia, whereas Radzi bin Abas et al.[4] report levoglucosan as the major organic compound detected in aerosol particulate matter during the haze episodes in Malaysia. Other authors (Zdráhal et al.,[30] Yttri et al.,[31] Puxbaum et al.[32]) reported high atmospheric levoglucosan concentrations in urban as well as rural sites in Europe during winter.

Although the studies citied above and many others present in the literature report that levoglucosan is the most important and abundant atmospheric biomass burning molecular tracer, a priority of this work was to verify the occurrence of mannosan and galactosan in the chromatographic peak obtained during ice analysis. In particular the total absence of any other peak besides that of levoglucosan at different chromatographic conditions (several different columns, varying the percentage of methanol in the mobile phase) and the contemporary low intensity of the m/z 161/87 and 161/129 transitions (that are principally due to the presence of galactosan and mannosan, respectively) confirm that the peak obtained from an Antarctic ice sample (Figure 1) is principally due to the presence of levoglucosan.

Levoglucosan is a very polar hydrophilic compound, and using methanol as an eluent in reverse chromatography caused a reduction in retention time, the loss of chromatographic separation (between levoglucosan, mannosan, and galactosan), and influenced the width of the chromatographic peak. So different

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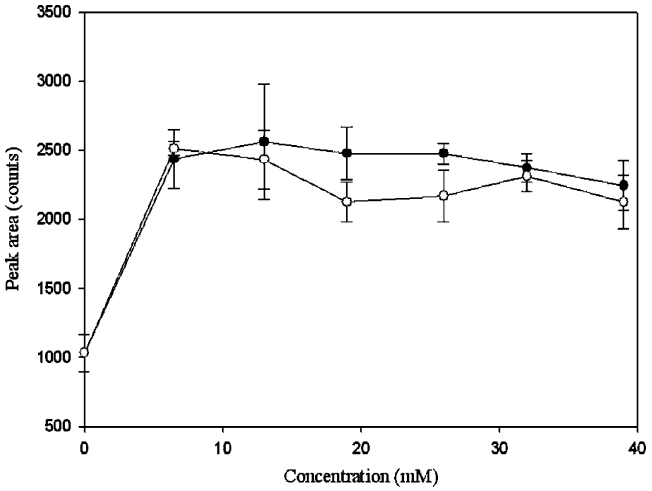

Figure 2. Influence of concentration and flow on the ammonia signal: ● 5 μL min^{-1}; ○ 10 μL min^{-1}.

aqueous solutions of methanol of 0%, 5%, 15%, 30%, and 50% v/v were tested as eluents for a standard solution of levoglucosan in ultrapure water. It has been observed that a lower methanol content leads to an increase in the retention time and a broadening of the peak, whereas a higher methanol content results in a reduction in the retention time and a narrowing of the peak; the best performance was obtained with a methanol concentration of 15% v/v, in the injected aqueous solution of levoglucosan. Also different types of water have been tested, and the results were that with the ultrapure water, produced in our laboratory as an eluent, the instrumental signal was about 70% higher than that obtained with HPLC/MS grade water (Romil Ltd., Cambridge, U.K.) probably due to differences in ion concentrations that influence the ionization of levoglucosan.

In order to optimize the instrumental signal and avoid contamination we directly introduced the melted sample into the HPLC instrument; this could have caused a possible alteration of the HPLC column, so we tested the use of a precolumn and the filtration of the sample. Use of a precolumn resulted in a 50% reduction of the instrumental signal, whereas filtration resulted in contamination of the sample. In order to test the filtration procedure the ultrapure water was filtered using Teflon filters (National Scientific, Rockwood, TN) that were washed in methanol and ultrapure water. The estimated levoglucosan concentration in the filtered ultrapure water was 24 pg mL^{-1} (three measurements; SD 28%), with values about double that of the ice core sample.

The mass spectrometric method performed with the ESI source resulted in the formation of $[M - H]^-$ ions at m/z 161, of which the signal was increased with a postcolumn infusion of an ammonium hydroxide solution. Several concentrations and flows of the ammonium hydroxide solution were tested: 6.5, 13, 19, 26, 32, and 39 mM, and flows of 5 and 10 μL min^{-1}, using a standard solution at 50 pg mL^{-1} of levoglucosan. The results are reported in Figure 2. We observed that generally the most intense signal was obtained using a flow of 5 μL min^{-1} and an ammonium solution of 13 mM.

Finally an alternative ionization technique, atmospheric pressure chemical ionization (APCI), was tested and optimized for the heated nebulizer source (Table 1), and the results were compared with the turbo ion spray source (ESI). For the same levoglucosan solution (10 ng mL^{-1}) a higher response was obtained with ESI than APCI by a factor of about 10.

Blank Contribution and Detection Limits. Special care was taken to evaluate the blanks in each step of the analytical procedure because of the extremely low concentration of levoglucosan in ice cores. In order to evaluate the possibility of levoglucosan contamination of the ice samples by the laboratory air, three cleaned LDPE vials (the volume was 800 μL) were left open in the normal laboratory (outside of any clean handling area) for 24 h and successively filled with 500 μL of ultrapure water, and the levoglucosan was quantified in the resulting solution. The results obtained show a concentration of levoglucosan that varied from 91 to about 212 pg mL^{-1}, which is about 10 times higher than the Antarctic ice samples (the blank was 3 pg mL^{-1}). This confirmed the need to decrease the number of treatment steps for sample preparation and to make a direct determination of levoglucosan in the sample.

Procedural blanks were evaluated by analyzing the levoglucosan in ultrapure water introduced into LDPE vials (six samples), which had undergone the cleanup treatment reported previously. The values obtained here have also been used to estimate the levoglucosan detection limit (LOD).

The LOD was quantified as 3 times the standard deviation of the procedural blanks ($n = 6$) with a mean value of 3 pg mL^{-1} (0.3 pg absolute amount injected). This value is lower than those reported in the literature for both GC/MS and LC/MS methods. In fact, in a recent review on the detection and quantification of levoglucosan in atmospheric aerosols, Schkolnik et al.[14] reported a method detection limit of 1×10^5 pg mL^{-1} using a GC/MS analytical procedure, an LOD of 6×10^4 pg mL^{-1} using ion chromatography with PAD, of 2.7×10^6 pg mL^{-1} using microchip capillary electrophoresis with PAD, and of 5×10^5 pg mL^{-1} using ion-exclusion chromatography with a photodiode array as detector. The same authors reported that ESI-MS methods showed the potential of being simpler and that they may also exhibit good sensitivity if used in combination with HPLC; in this study we can confirm that HPLC/ESI-MS/MS shows excellent results in terms of LOD and sensitivity.

The LOD is in general lower than the minimum levoglucosan concentrations detected in glacial Antarctic ice samples, whereas it is comparable with concentrations detected in interglacial ice samples, confirming on one hand the extreme sensitivity of the HPLC/ESI-MS/MS with triple quadrupole mass spectrometry for the analysis of levoglucosan present at the ultratrace level and on the other, the great difficulty of these types of analysis, for extreme attention must be paid to avoid contamination in all steps of the analytical procedure.

Calibration. In this work the internal standard method has been used for the determination of levoglucosan in Antarctic ice. The internal standard method was performed by isotope dilution comparing the native compound peak area with that of the ^{13}C6-labeled isotopomer. Results were corrected for the instrumental response factor, which was evaluated by analyzing a solution containing levoglucosan at a concentration of 50 pg mL^{-1} and ^{13}C-labeled levoglucosan at 50 pg mL^{-1} concentration in ultrapure water.

An external standard calibration was used to study potential matrix effects. The external standard calibration method was performed using calibration curves obtained by adding different amounts of levoglucosan standard spikes to ultrapure water. A parent standard solution of levoglucosan in ultrapure water (4.46 mg mL^{-1}) was prepared from the levoglucosan reagent and successively diluted to 440 pg mL^{-1} in ultrapure water. From this solution, stock standard solutions of levoglucosan in ultrapure water were prepared with concentrations of 13, 17, 32, 47, 61, and 73 pg mL^{-1}. The parent solution and the stock standard solutions were stored at 4 °C in LDPE bottles. Good linearity was obtained, with an R^2 value of 0.9817, a slope value of 101 287 counts/(pg μL^{-1}), and an intercept value of 196.84 counts.

The standard addition method was performed by calibration curves obtained by adding different amounts of a previous parent standard solution of levoglucosan to three aliquots of a melted Antarctic ice sample collected at Dome C at a depth of 2721.4 m (dated 401.631 kyr BP). The levoglucosan concentrations in the final standard solutions were 13, 17, 47, and 73 pg mL^{-1}. In this linear range calibration curves were obtained with R^2 of 0.9980, a slope value of 101 878 counts/(pg μL^{-1}), and an intercept value of 103.02 counts. The signal intensity and slope observed for the external calibration method were comparable to those obtained for the standard addition method, so we can suppose that possible matrix effects were not present.

Repeatability and Accuracy. An estimation of the repeatability of the method was obtained from five consecutive measurements of the inner core (see below) of the Antarctic ice samples. The relative standard deviation ranges from 20% for a levoglucosan concentration of 20 pg mL^{-1} to 50% for a concentration of 9 pg mL^{-1}. These standard deviations are in general higher than those reported in the literature in aerosol samples for both GC/MS methods[11] (2−20%) and HPLC[7] (6.7%). In addition, the excellent linearity obtained for the above-mentioned calibration is an indication in itself of good precision.

Estimating the accuracy for ultratrace determinations at the picogram per milliliter is a difficult task, due to the numerous sources of error and especially because of the lack of a certified reference material. To estimate the accuracy of the method, we carried out a recovery test on the six melted Antarctic ice samples by adding standard spikes of a levoglucosan solution. The levoglucosan recovery measured in the spiked samples (17 pg mL^{-1}) was found to be 95%.

Levoglucosan Concentration in Antarctic Ice Sample. Initially it was necessary to check whether the drilling fluid and the handling operations performed in the field had contaminated the core with levoglucosan and whether or not this contamination had reached the innermost parts of the core. Levoglucosan concentrations were determined in three outer layers and in the inner core of the ice sections. A concentration plateau, in at least two consecutive layers of the central part of the core, indicates that these inner parts are free from the outside contamination; the plateau value then represents the original concentration in the ice core. If, on the contrary, a continuous decrease of concentration is observed toward the center, it confirms that outside contamination has penetrated to the center of the core. The concentration of the inner part will then represent an upper limit of the real concentration in the original ice. Figure 3 shows the radial concentration profile with a comparison with the LOD value obtained for a glacial period Antarctic ice core collected at a depth of 2396.8 m and for an interglacial Antarctic ice core collected at a depth of 2721.4 m drilled at Dome C and dated, respectively, between 274.1 and 401.6 kyr BP. It can be noted that the levoglucosan concentration in the inner core and in the external layers shows a variation by a factor of between about 2 and 7. However, it is interesting to note that there is a concentration plateau for the internal layers analyzed, showing that contamination from the outside has not penetrated into the central part of the core.

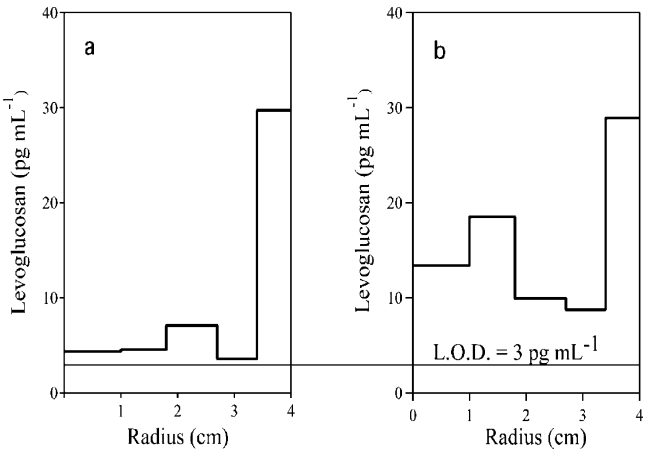

Figure 3. Radial concentration profile of levoglucosan for Antarctic ice cores sections from interglacial (a) and glacial (b) periods.

Levoglucosan concentrations are extremely low even in the outermost layers of both the EPICA ice core sections. Thus, on account of the very low levoglucosan contamination in the drill fluid and the careful precautions taken after sampling and during decontamination, any possible additional contamination deriving from the drill fluid does not affect the innermost parts of the core sections.

As reported above, the ice core samples selected to test the developed method are two samples from the last glacial age and from the last interglacial period. The levoglucosan concentration in the ice core sample from an interglacial period showed a lower concentration (about 3 times) than that from a glacial age (Figure 3).

To our knowledge these are the first levoglucosan concentrations reported in Antarctic ice samples. Other tracers such as oxalate, glycolate, and acetic and formic acids have also been employed as biomass burning signatures in the polar ice,[22] but levoglucosan has the merit of being a specific molecular marker of cellulose burning in the paleorecord.

The explanation for higher concentrations of levoglucosan in Antarctic ice samples during the glacial period can be mainly related to the much greater input of continental dust at high latitudes during this period and consequently to a higher transfer of levoglucosan from temperate zones to polar regions. The large increase in continental aerosol fallout to the East Antarctic plateau during glacial periods was produced essentially by three concomitant factors. First, decreased seawater evaporation reduced the strength of the hydrological cycle, thus decreasing the scavenging process of aerosol particles from the atmosphere. Second, an increased storage of water in the form of ice in the

polar ice caps caused a lowering of the sea level, exposing a larger portion of the continental shelves to wind erosion. Finally, the enhanced thermometric and barometric gradients between low and high latitudes strengthened poleward atmospheric circulation and continental aerosol transport. The combination of these factors augmented the number of aerosol particles mobilized from the surface of the continents, causing a longer atmospheric residence time, and elongating their trajectories, therefore enhancing their global transport and continental aerosol fallout over the polar ice caps.[24,25] Therefore, the transport of atmospheric particulates seems to be greater or more efficient during glacial periods compared to the interglacial period. Given that levoglucosan has been proposed as a single tracer species for wood smoke, and is the most abundant single compound identified in atmospheric fine particulate matter samples from regions affected by biomass burning, the results obtained in this study, although indicating that a higher number of samples should be analyzed, demonstrate the possibility of identifying the impact of biomass burning on aerosols during different climatic periods.

CONCLUSION

A method for the direct determination of levoglucosan in Antarctic ice is reported. This analytical method has the advantage of avoiding sample contamination during the preanalytical procedure. The method based on HPLC/(−)ESI-MS/MS has been optimized providing excellent LODs that allow the determination of the extremely low concentration (picogram per milliliter) of levoglucosan in ice cores.

This work demonstrates lower concentrations of levoglucosan in Antarctic ice from an interglacial period compared to that from the glacial period. This highlights the possibility of a link between biomass burning emissions and climate change.

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