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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MAY 2005

Impact Factor: 5.33 · DOI: 10.1021/es048363c · Source: PubMed

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Environ. Sci. Technol. **2005**, *39,* 2744−2752

New Analytical Method for the Determination of Levoglucosan, Polyhydroxy Compounds, and 2-Methylerythritol and Its Application to Smoke and Rainwater Samples

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Biomass burning is an important source of smoke aerosol particles, which contain water-soluble inorganic and organic species, and thus have a great potential of affecting cloud formation, precipitation, and climate on global and regional scales. In this study, we have developed a new chromatographic method for the determination of levoglucosan (a specific tracer for biomass burning particles), related polyhydroxy compounds, and 2-methylerythritol (recently identified as isoprene oxidation product in fine aerosols in the Amazon) in smoke and in rainwater samples. The new method is based on water extraction and utilizes ion-exclusion high-performance liquid chromatography (IEC−HPLC) separation and spectroscopic detection at 194 nm. The new method allows the analysis of wet samples, such as rainwater samples. In addition, aliquots of the same extracts can be used for further analyses, such as ion chromatography. The overall method uncertainty for sample analysis is 15%. The method was applied to the analysis of high-volume and size-segregated smoke samples and to rainwater samples, all collected during and following the deforestation fires season in Rondônia, Brazil. From the analysis of size-segregated samples, it is evident that levoglucosan is a primary vegetation combustion product, emitted mostly in the 0.175−1 μm size bins. Levoglucosan concentrations decrease below the detection limit at the end of the deforestation fires period, implying that it is not present in significant amounts in background Amazon forest aerosols. The ratio of daytime levoglucosan concentration to particulate matter (PM) concentration was about half the nighttime ratio. This observation is rationalized by the prevalence of flaming combustion during day as opposed to smoldering combustion during night. This work broadens the speciation possibilities offered by simple HPLC and demonstrates the importance of multianalysis of several kinds of samples for a deeper understanding of biomass burning aerosols.

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Introduction

Aerosols from biomass burning have recently been the focus of increasing attention for their role in atmospheric chemistry and climate (*1*−*3*). Smoke particles may affect the climate directly due to their ability to absorb and scatter light (*1*, *4*−*7*), indirectly by altering cloud properties, since they act as cloud condensation nuclei (CCN), and semidirectly due to their light absorption properties (*6*, *8*−*10*). Clouds and precipitation on a regional scale were found to be affected by biomass burning aerosols (*6*, *10*−*13*). The interaction between biomass burning aerosols and clouds may also lead to an increase in stratospheric water vapor content (*12*). Biomass burning aerosols consist of a complex mixture of organic and inorganic compounds. Water-soluble organic compounds (WSOC) may account for 40−74% of the smoke particles' total carbon (*14*), and it is this part of the aerosol which has a significant role in determining its properties as a CCN.

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a dehydrated glucose containing a ketal functional group that accounts for 2−8% of WSOC mass in Amazonian smoke samples (*14*). It is produced during cellulose pyrolysis (Figure 1) and emitted in fine smoke particulate matter (*15*−*17*). Thus, it is utilized as a specific tracer for emissions from vegetation combustion in atmospheric particulate matter. Combustion of non-biomass materials (i.e., fossil fuels) or biodegradation and hydrolysis of cellulose do not produce levoglucosan (*18*). Levoglucosan is relatively stable in the atmosphere, allowing long-range transport (*19*). Hence, it is highly desirable to be able to quantify levoglucosan in rainwater and smoke samples, both for source assignment purposes and as part of the WSOC characterization effort.

Recently, Claeys et al. (*20*, *21*) have identified 2-methylerythritol and 2-methylthreitol in background aerosol particles from Amazonia. It was suggested that these diastereomeric five-carbon compounds are formed through the liquid-phase oxidation of isoprene by hydrogen peroxide and account for ∼2% of the fine (<2.5 μm) organic carbon measured suggesting that they may significantly contribute to secondary organic aerosol formation (*21*). Efficient methods for the quantification of these new species in further studies are therefore desirable.

The most common analytical method for the determination of levoglucosan, other polyhydroxy compounds, and 2-methylerythritol in atmospheric particles involves extraction of the sample into an organic solvent system (CH_2Cl_2−methanol 80:20, v/v), derivatization with a silylation reagent (bis(trimethylsilyl)trifluoroacetamide), which requires very dry (anhydrous) conditions, followed by GC/MS analysis (*15*, *22*). The method is sufficiently sensitive for measuring background levels of levoglucosan. However, it is quite complex and requires a long preparation time, as well as relatively sophisticated and expensive analytical facilities. This method cannot be applied to wet samples, let alone to the analysis of rainwater. Another method recently developed by Gao et al. (*23*) consists of electrospray-MS (ESI-MS) analysis in parallel with ion chromatography−pulsed amperometric detection (IC−PAD). The method is complicated by the use of two parallel analytic devices and has a detection limit of 0.02 $\mu g/m^3$. Graham et al. (*14*) have determined levoglucosan in water-extracted smoke samples, using both

10.1021/es048363c CCC: $30.25

Published on Web 03/15/2005

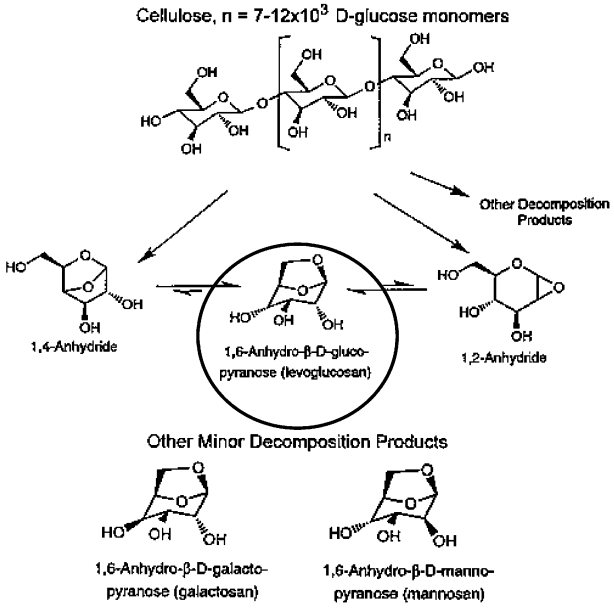

FIGURE 1. 1,6-Anhydro-β-D-glucopyranose (levoglucosan) (circled) is an abundant product of cellulose combustion at $t > 300$ °C (*17*).

GC/MS and a method based on HNMR detection, which as yet has not been validated with respect to levoglucosan (*24*).

Here, we describe the development of a new method which is based on ion-exclusion chromatography (IEC) and allows detection and quantification of levoglucosan and other polyhydroxy compounds in rainwater and water-extracted smoke samples. This is a relatively simple method which is based on water extraction of these species. Aliquots of the same sample extract may be used for further ion chromatographic analyses. The application of the new method to the analysis of smoke particles and to rainwater samples from Amazonia is reported, and conclusions are drawn as to the use of levoglucosan as a biomass burning tracer.

Experimental Section

Materials. Perchloric acid solution (10 mM) was used as an eluent for the liquid chromatography. The eluent was prepared from perchloric acid 70% (AnalaR, BDH Laboratory Supplies, Pool, England). Standards used were 1,6-anhydro-β-D-glucopyranose (levoglucosan) ≥98.0% and D(+)-arabitol ≥99% (Fluka Chemie, GmbH), *meso*-erythritol (Aldrich Chemical Co., Wisconsin, United States), D(−)-mannitol 98−101% (Riedel-de Haën, Sigma Aldrich GmbH), 1,6-β-D-mannopyranose (mannosan) ~98% (Sigma, MO), and D-glucose (AnalaR BDH Laboratory Supplies, Pool, England). A mixture of 2-methylthreitol and 2-methylerythritol, synthesized by the University of Antwerp (*20*), was used as a standard. All water used had resistivity of 18.2 ± 0.1 MΩ-cm.

Sampling. Smoke samples were collected in the Amazon during the deforestation fires season. Sampling took place at the Fazenda Nossa Senhora Aparecida pasture site, in Rondônia, Brazil, September and October 2002, in the framework of the LBA-SMOCC (The Large Scale Biosphere-Atmosphere Experiment in Amazonia—Smoke Aerosols, Clouds, Rainfall, and Climate: Aerosols from Biomass Burning Perturb Global and Regional Climate) field campaign. All samples were collected for 12 h for high loading and 24 h for cleaner conditions. High-volume (HiVol) samples were collected by the Institute for Nuclear Sciences, Ghent University (UGent), Belgium, using a high-volume dichotomous sampler with two size fractions, out of which the fine size fraction (<2.5-μm aerodynamic diameter) was analyzed. Pallflex filters (Gelman, Pall Corporation, NY) were used. The flow rate through the fine fraction filter (converted to 25 °C, 1 bar) was typically 19 m^3/hr, and it passed through a 61.5 cm^2 filter surface area. All filters were baked overnight at >500 °C prior to sampling to eliminate organic contamination. During sampling, a back filter was placed behind the sample filter to assess sampling artifacts in aerosols collection (*25*), such as gas-phase species that adsorb on both filters. Samples were stored at −25 °C in prebaked aluminum foil envelopes. Some additional samples used only for method development were collected in Rehovot, Israel, on May 10−11, 2001, during a national bonfire festival in Israel. They were collected on Gelman Quartz Microfiber (QF) filters (Gelman, Pall Corporation, NY) using a commercial high-volume sampler.

Size-resolved samples were collected by the Institute of Physics, University of São Paulo (IFUSP), São Paulo, Brazil, using a microorifice uniform deposit impactor (MOUDI) (model 110, MSP corporation, Minneapolis, MN), on Nuclepore Polycarbonate filters (Whatman, New Jersey) of 47-mm diameter, at a flow rate of 25 L/min. Aerosols of aerodynamic diameter less than 18 μm were separated into nine stages with calibrated aerodynamic cutoffs of 18, 10.0, 3.2, 1.8, 1.0, 0.56, 0.33, 0.175, and 0.093 μm. The inlet stage was not analyzed in this study. The loaded filters were placed immediately in clean plastic Petrislides and stored in the dark at −18 °C until analysis. Field blanks were obtained using the same loading and unloading procedure as for normal filters but with a sampling time of only 15 s.

Rainwater sampling was performed from 12 September to 10 November using a wet-only Aerochem-metrics sampler. Rain was collected in high-density polyethylene bottles on an event basis and stored immediately after collection. Thymol was added to the bottles prior to sampling to preserve organic species from bacterial activity. The samples were stored in the darkness under refrigeration until analysis.

Sample Preparation. *Extraction.* Each HiVol sample (approximately 15 cm^2) was extracted twice into 5.0 mL of water by short vortex agitation followed by 15 min of gentle shaking. The combined extract was centrifuged for 5 min and filtered through a GHP Acrodisk syringe filter (25 mm, 0.45-μm pore size, Gelman, Pall Corporation, NY), which was previously washed with 10 mL water. MOUDI samples were extracted in the same manner into 4.0 mL of water. These were filtered using a GHP Acrodisk syringe filter (13 mm, 0.45-μm pore size). It has been validated that further extraction was not needed. Rainwater samples were concentrated by a factor of 3−12 under nitrogen flow, at 30 °C, and were then directly injected.

Solid-Phase Extraction (SPE). Polyacidic humic-like substances (HULIS) are present in smoke samples from Amazon forest fires (*26*). Since these compounds are negatively charged, they are eluted in the void volume of the ion-exclusion column (see below), and due to their strong light absorption, they form a huge unresolved peak in the beginning of the chromatogram. The big tail of this peak interferes greatly with the detection of the neutral polyhydroxy compounds, and to avoid that, the polyacids must be selectively removed. Therefore, each sample (both rainwater and filter extracts) was passed through an Accell QMA SPE anion exchange cartridge (Waters, MA), which retains dissociated acids, such as the HULIS, but not neutral compounds, such as polyhydroxy compounds. This was done according to sample size: Plus cartridges (internal volume 0.8 mL) were used for the larger HiVol and rain samples, while Light cartridges (internal volume 0.4 mL) were used for the smaller MOUDI samples. Each Plus cartridge was prewashed with 6 mL of water, and then 4.0 mL of the sample was passed through it. A levoglucosan retention test was conducted for the SPE cartridges. It was found that the first 0.5 mL eluting from Plus SPE cartridges do not contain levoglucosan (due to the cartridge's dead volume). Hence,

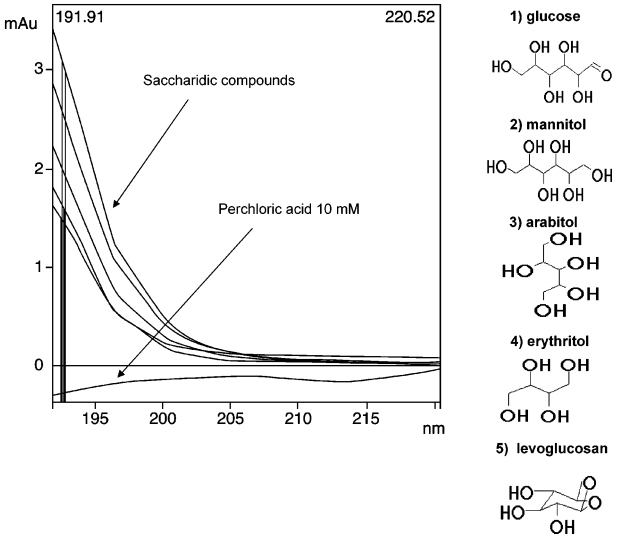

FIGURE 2. Absorption spectra of glucose, mannitol, arabitol, erythritol, and levoglucosan (polyhydroxy compounds) and of the eluent, perchloric acid 10 mM. As one can see from the figure, within our detector's range the polyhydroxy compounds show high absorption at 194 nm, where the eluent has insignificant absorption.

it was discarded and the next 3.5 mL plus an additional 1 mL of water that was passed through the cartridge was collected for each sample. Each Light cartridge was prewashed with 3.5 mL of water, and then 1.5−2.3 mL of the sample was passed through it. Since the dead volume of these Light SPE cartridges is very small, as was verified in a levoglucosan retention test, the entire sample was collected, along with an additional 0.5 mL of water.

IEC−HPLC−PDA Analysis. Chromatographic separation of polyhydroxy compounds (anhydrosugars, sugar alcohols, polyols, etc.) was achieved by ion-exclusion chromatography (IEC) in a poly(styrene-divinylbenzene) sulfonate (H^+) cation-exchange resin column (Dionex, IEC-AS1). Unlike ion-exchange chromatography, in IEC the charge of the functional groups on the ion-exchange resin has the same sign as that of the analytes. In other words, weak acids, alcohols, and carbohydrates are separated on a cation-exchange resin in the H^+ form, using an acidic eluent, by a hydrophobic adsorption−retention mechanism (*27*). In IEC, strong acids, being highly ionized, pass quickly through the column, while nonionic compounds can enter the resin network and elute in order of decreasing acidity (*27*, *28*). The development of the IEC separation procedure applied in this study is based on the Dionex application note for separation of aliphatic alcohols on an ICE-AS1 column, utilizing 50 mM perchloric acid as eluent at 0.8 mL/min flow rate (*40*). According to the IEC principles, aliphatic alcohols which contain several hydroxyl groups are eluted in order of decreasing number of hydroxyl groups (i.e., decreasing acidity).

A Varian ProStar 230I HPLC pump, a Varian ProStar 410 autosampler, and a Varian ProStar 330 photodiode array (PDA) detector were used. The aim of the procedure development was to optimize separation between glucose, mannitol, arabitol, erythritol, 2-methylerythritol, 2-methylthreitol, and levoglucosan (polyhydroxy compounds hereafter). The retention of the polyhydroxy compounds was constant for eluent (perchloric acid) concentrations ranging between 10 and 100 mM. Therefore, elution was performed with 10 mM perchloric acid at 1 mL/min flow rate. Two columns were sequentially connected to improve separation. To minimize peak widths and stabilize the baseline, the columns were thermostated at 26 ± 0.5 °C. At 194 nm, the polyhydroxy compounds have sufficient absorption, while the eluent's absorption is very low (Figure 2).

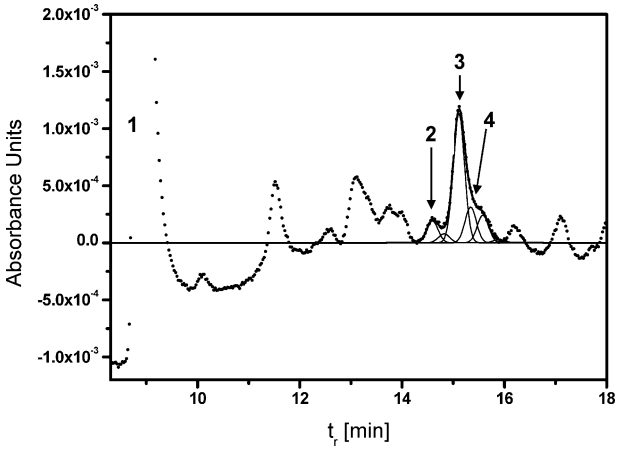

FIGURE 3. Chromatogram of a high-volume PM2.5 smoke sample, collected in Rondônia, Brazil, during the deforestation fire season. The peaks: (1) the remains of the HULIS front peak, (2) 2-methylerythritol, (3) levoglucosan, and (4) mannosan, a stereoisomer of levoglucosan, that appears as a shoulder on the levoglucosan peak.

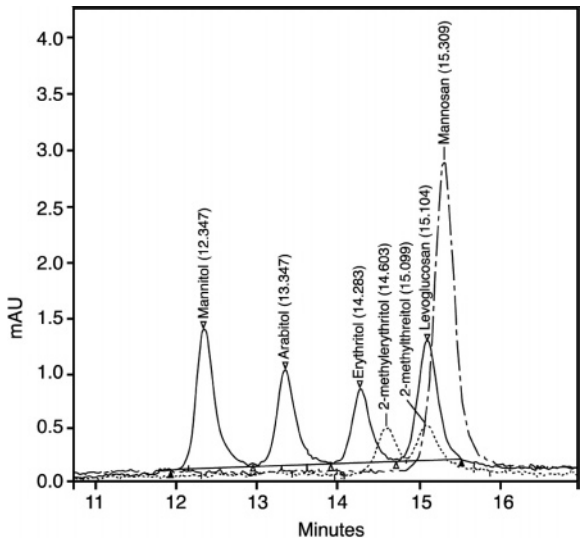

FIGURE 4. Three chromatograms demonstrating standard separation obtained by the method. Solid line: mannitol, arabitol, erythritol, and levoglucosan (in that order) are well separated (chromatographic resolution, $R > 3.0$). Dashed line: mannosan, a stereoisomer of levoglucosan, which can be separated from levoglucosan by multiple-Gaussian peaks fit analysis. Dotted line: 2-methylerythritol (left) is separated from levoglucosan ($R = 1.7$), while 2-methylthreitol (right) is not separated from levoglucosan. The coelution of 2-methylthreitol with levoglucosan must be considered in calculations.

Integration of the chromatograms was performed using the Origin graphics program by multiple-Gaussian-fit analysis after baseline subtraction. A typical smoke sample chromatogram obtained by the method is shown in Figure 3. As can be seen in the figure, the front HULIS peak (peak 1) is large even after SPE treatment. Without the use of SPE, this peak covers most of the peaks seen in the chromatogram.

Validation. *Chromatographic Separation and Levoglucosan Determination.* Glucose, mannitol, arabitol, erythritol, and levoglucosan are well separated (Figure 4) with $R > 3.0$, (R is the chromatographic resolution, which is defined as the ratio between twice the distance between two peaks and the sum of their widths at half-height) (*29*). 2-Methylerythritol is separated from levoglucosan with $R = 1.7$. However, levoglucosan coelutes with 2-methylthreitol, and this must be taken into account in the quantitative analysis. Mannosan,

a stereoisomer of levoglucosan, appears as a shoulder on the levoglucosan peak (Figure 3) and is resolved using the multiple-Gaussian peaks fit analysis.

Coelution Correction. The University of Antwerp team has shown that the ratio between the two 2-methyltetrol stereoisomers in smoke samples is almost constant (*41*). The ratio deduced from the analysis of HiVol samples collected in parallel to the ones reported in this paper, during the SMOCC campaign, is 2-methylthreitol/2-methylerythritol = 0.34 ± 0.07. Therefore, to compensate for the coelution of levoglucosan with 2-methylthrietol, we have subtracted 0.34 of the 2-methylerythritol peak area from the levoglucosan peak area. This correction is typically 4% of the levoglucosan signal.

Linearity, Limit of Detection (LOD), Limit of Quantification (LOQ), and Blank Control. The linear range of levoglucosan detection is between 2.5 μg/mL and 25 μg/mL (R^2 = 0.9993 for the regression in the linear range). The limit of detection (LOD) is 0.5 μg/mL with signal-to-noise ratio (S/N) = 3 for five repetitions. The limit of quantification (LOQ) is 1 μg/mL, with S/N = 4.5 and %RSD = 9% for 11 repetitions.

Blanks. For all the steps of the procedure, blank measurements were conducted. All blanks, including lab blanks, sampling field blanks, and HiVol sampler back filters, showed no levoglucosan.

Recovery. *Recovery Test and Levoglucosan Stability.* To determine the efficiency of the extraction from smoke samples, the recovery of the entire procedure was verified by spiking quartz fiber filters with 10 μg levoglucosan standard and then subjecting them to the described procedure. On the basis of eight replicates, the recovery obtained was 95 ± 3%.

Since we utilize water extraction, the same extract used for levoglucosan determination was also used for ion chromatographic analysis. For this reason, samples were not always analyzed immediately after extraction, and the extracts were stored in refrigeration (2−4 °C) for 1−8 weeks. Levoglucosan standards were stored under the same conditions to test levoglucosan stability. No significant loss of levoglucosan during storage was observed.

Precision. The maximum RSD obtained for repeated injections of the same standard solution of levoglucosan (concentration 2 μg/mL) was 6% for five injections.

To determine the precision obtained for several extractions of the same sample filter, we used a sample collected in Israel during a national bonfire festival on May 10−11, 2001. The sample was divided into six parts and the same procedure was repeated for each part. The precision obtained was RSD = 3.3%. Since the deviation between injections of the same extract is 9%, larger than the deviation between fractions of the same filter, we take the overall sample RSD to be 9%.

Overall Method Uncertainty. The method uncertainty for detection of a standard is 6%, which is the worst-case precision of standard detection. In real smoke samples, additional sources for uncertainty must be considered, including (1) the analytical procedure uncertainty, including the injection precision of both standard and sample solutions and the recovery uncertainty, and (2) the uncertainty of the correction needed due to the coelution of levoglucosan with 2-methylthreitol.

The method's uncertainty in levoglucosan concentration, prior to the coelution correction, was 11%. The coelution correction adds 4%. Thus, the overall uncertainty of levoglucosan determination in smoke samples is 15% for concentrations greater than LOQ. For concentrations that lie between LOQ and LOD, an uncertainty of 23% is assigned. All method validation parameters are summarized in Table 1.

Applicability of the Method. The new method employs shorter sample preparation times and is simpler than the existing derivatization−GC/MS method. Since it utilizes water extraction, it retrieves the fraction pertinent to CCN formation and allows the analysis of wet samples such as rainwater and cloud droplets. Ion chromatography can be further carried out on the same extracts.

TABLE 1. Summary of the Method's Validation Parameters

linearity range	2.5−25 μg/mL
limit of detection	0.5 μg/mL
limit of quantification	1 μg/mL
recovery	95 ± 3%
precision (standard)	6%
precision (smoke sample)	9%
overall method uncertainty (for concentrations > LOQ)	15%

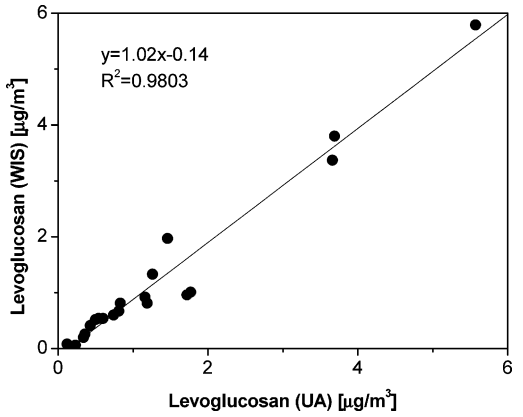

FIGURE 5. A comparison between levoglucosan values obtained using the method described in this paper (*y*-axis), and with values obtained using the silylation−GC/MS method (Claeys, unpublished data, *x*-axis) for samples collected in parallel. The correlation slope is 1.02 ± 0.05, and the intercept is at −0.14 ± 0.09. R^2 = 0.9803.

The main drawback of this method in comparison to the GC/MS method is its lower sensitivity. The GC/MS method can detect levoglucosan in background aerosols while this method is as yet unable to. Sensitivity may be increased by further concentrating water extracts and by using SPE cartridges with smaller internal volumes. Another issue is the coelution of levoglucosan with other species, which was overcome in this work by the integration technique and by a priori knowledge about the ratio between the 2-methyltetrol diastrereomers. Further investigation of this ratio in different conditions is therefore desirable to reduce the portion of method uncertainty caused by the uncertainty in this ratio. Since these compounds have been just recently discovered in aerosols (*20*), it is to be expected that such information will soon follow. Finally, due to both separation and sensitivity issues, this method cannot be used to quantify mannosan and galactosan, levoglucosan's stereoisomers, emitted in much smaller quantities than levoglucosan (*30*) and glucose (due to coelution with a component from the SPE cartridges), a biogenically emitted compound.

In view of the merits and shortcomings of the new method, it is suggested that the derivatization−GC/MS method is most suitable for individual quantification of each polyhydroxy compound in a small amount of samples, which may include either smoke or background aerosols. In contrast, the new IEC−HPLC method is most suitable for quantifying levoglucosan or 2-methylerythritol, combined with full ion analysis of a large amount of samples collected under smoky or semismoky conditions or of wet samples such as rainwater and cloud droplets. In the next section, such a multisample integrated analysis is demonstrated.

Method Application: Results and Discussion. High-Volume Samples. During the LBA-SMOCC field campaign,

TABLE 2. Levoglucosan Concentrations in High-Volume PM2.5 Smoke Samples Collected during the SMOCC Campaign[b]

sample name	start time GMT (2002)		end time GMT (2002)		levoglucosan [μg/m^3]	% levoglucosan carbon of WSOC	PM2 [μg/m^3]	K^+ [μg/m^3]
R2HIV03D	Sept 11	12:38	Sept 11	21:42	0.08	0.7	16.6	0.39
R2HIV03N	Sept 11	22:15	Sept 12	11:40	0.15	1.6	18.2	0.47
R2HIV04N	Sept 12	22:22	Sept 13	11:36	1.14	3.5	61.2	1.28
R2HIV05D	Sept 13	12:29	Sept 13	21:45	0.09	0.5	23.0	0.54
R2HIV05N	Sept 13	22:21	Sept 14	11:37	2.65	5.7	90.6	1.43
R2HIV06D	Sept 14	12:14	Sept 14	21:16	0.81	3.3	39.7	0.49
R2HIV06N	Sept 14	22:28	Sept 15	10:51	0.60	3.1	34.6	0.16
R2HIV07D	Sept 15	11:27	Sept 15	21:45	0.34	1.5	32.1	0.54
R2HIV07N	Sept 15	22:30	Sept 16	10:58	0.53	2.5	34.9	0.55
R2HIV09D	Sept 17	11:45	Sept 17	21:45	1.34	4.0	79.9	1.04
R2HIV09N	Sept 17	22:45	Sept 18	11:00	3.37	6.2	94.9	1.74
R2HIV10D	Sept 18	12:45	Sept 18	21:40	0.67	2.2	49.5	1.01
R2HIV10N	Sept 18	22:50	Sept 19	11:00	3.81	6.4	111.4	1.78
R2HIV11D	Sept 19	12:40	Sept 19	21:45	0.93	1.9	70.7	1.27
R2HIV11N	Sept 19	22:30	Sept 20	11:00	5.80	7.1	141.9	2.41
R2HIV14D	Sept 22	11:45	Sept 22	21:45	0.86	1.8	74.9	1.03
R2HIV14N	Sept 22	22:30	Sept 23	11:00	0.67	1.1	95.7	1.16
R2HIV15D	Sept 23	11:45	Sept 23	22:00	1.03	1.8	85.2	1.45
R2HIV15N	Sept 23	22:45	Sept 24	11:00	0.98	2.3	65.5	1.25
R2HIV16N	Sept 24	23:00	Sept 25	11:00	1.13	3.4	54.4	0.95
R2HIV17D	Sept 25	13:00	Sept 25	22:45	1.98	2.4	116.1	1.99
R2HIV17N	Sept 25	23:00	Sept 26	11:00	1.70	1.8	139.7	2.08
R2HIV18D	Sept 26	11:50	Sept 26	21:45	0.34	0.8	63.8	1.18
R2HIV19D	Sept 27	12:00	Sept 27	21:45	0.17	0.7	34.0	0.61
R2HIV19N	Sept 27	22:30	Sept 28	11:00	0.20	0.9	42.3	0.61
R2HIV20N	Sept 28	23:30	Sept 29	11:00	0.22	2.6	12.6	0.33
R2HIV21	Sept 29	12:15	Sept 30	11:00	0.11	1.2	15.8	0.29
R2HIV24D	Oct 2	13:15	Oct 2	21:45	0.23	1.2	28.8	0.58
R2HIV24N	Oct 2	22:48	Oct 3	11:00	0.94	3.1	55.4	1.02
R2HIV26D	Oct 4	12:00	Oct 4	21:45	0.80	2.6	46.1	0.71
R2HIV26N	Oct 4	22:45	Oct 5	11:00	4.17	7.0	109.6	1.88
R2HIV29D	Oct 7	12:00	Oct 7	21:45	0.21	0.7	40.5	0.75
R2HIIV29N	Oct 7	22:30	Oct 8	9:10	0.32	1.1	48.0	0.77
R2HIV30	Oct 8	14:15	Oct 9	11:00	0.11	1.7	8.6	0.13
R2HIV32	Oct 10	12:00	Oct 11	11:00	0.09	1.0	14.3	0.26
R2HIV35D	Oct 13	12:15	Oct 13	21:45	0.03	0.2	18.6	0.47
R2HIV35N	Oct 13	22:15	Oct 14	11:00	0.33	1.9	24.7	0.53
R2HIV39	Oct 17	12:15	Oct 18	11:00	0.54	3.1	28.8	0.52
R2HIV40	Oct 18	12:00	Oct 19	11:00	0.53	3.0	29.9	0.6
R2HIV41	Oct 19	12:00	Oct 20	10:40	0.26	2.1	18.3	0.3
R2HIV43N[a]	Oct 21	23:30	Oct 23	11:00	0.17	1.7	15.6	0.31
R2HIV44D[a]	Oct 23	13:00	Oct 24	22:00	<LOD	0	13.7	0.31
R2HIV45N[a]	Oct 24	23:00	Oct 26	11:00	0.19	1.7	18.4	0.39
R2HIV46D[a]	Oct 26	12:00	Oct 27	22:00	0.05	0.4	22.2	0.77
R2HIV48D[a]	Oct 29	15:30	Oct 30	22:00	0.08	0.8	13.5	0.25
R2HIV49N[a]	Oct 30	23:30	Nov 1	11:00	0.08	3.7	4.3	0.1
R2HIV54	Nov 10	12:30	Dec 11	12:50	<LOD	0	2.3	0.03

[a] Sampled for two consecutive days (D) or nights (N). [b] Levoglucosan was determined using the method reported in this paper, and K^+ using IC, by the Weizmann Institute Team. WSOC and PM2 were determined for samples collected in parallel by the UGent Team. The uncertainty for levoglucosan is 15%.

particle samples were collected by the Institute for Nuclear Sciences, Ghent University (UGent), Ghent, Belgium, using two high-volume dichotomous samplers (named R1HiVo and R2HiVo) in parallel. These samples were analyzed for OC by the UGent, and the OC values from the two samplers agreed very well (mean ratio = 0.97 ± 0.10). For the OC determination method, see Schmid et al. (*31*). Samples from R2HiVo were analyzed by the newly developed method, while samples from R1HiVo were analyzed by the Department of Pharmaceutical Sciences, University of Antwerp, Belgium, using the silylation−GC/MS method (*22*). The results obtained for the parallel samples (*41*) by the two methods agree well, with a slope of 1.02 ± 0.05, intercept at -0.14 ± 0.9, and $R^2 = 0.9803$ (Figure 5). This comparison is confirmatory to the validity of the new method reported here. Table 2 summarizes the results obtained from the analysis of the R2HiVo samples.

A time series of the levoglucosan results is shown in Figure 6a. During the dry period (September 14 to October 7, 2002), when deforestation fires were most intense, high levels of levoglucosan were measured (0.08−5.9 μg/m^3). During the transition period to the wet season (October 7−30, 2002), levoglucosan levels in regional haze particles decreased to 0.03−0.55 μg/m^3. Wet period samples were analyzed as well, but levoglucosan levels were below LOD, implying that levoglucosan is not present in significant concentrations in background aerosols at the Amazon basin after the biomass burning activity has ceased. Levoglucosan concentration in back filters were below detection limit for all periods, implying that it is an aerosol-bound species, which is not present in the gas phase, and that fine particles did not penetrate through the front filter.

Inorganic and organic ionic species in the same samples were also analyzed (*32*). A correlation between levoglucosan and K^+ concentrations is shown in Figure 6b. K^+ was chosen because it is widely considered as a biomass burning marker. During daytime, levoglucosan/K^+ ratios are smaller than during night. It is suggested that during daytime, when the

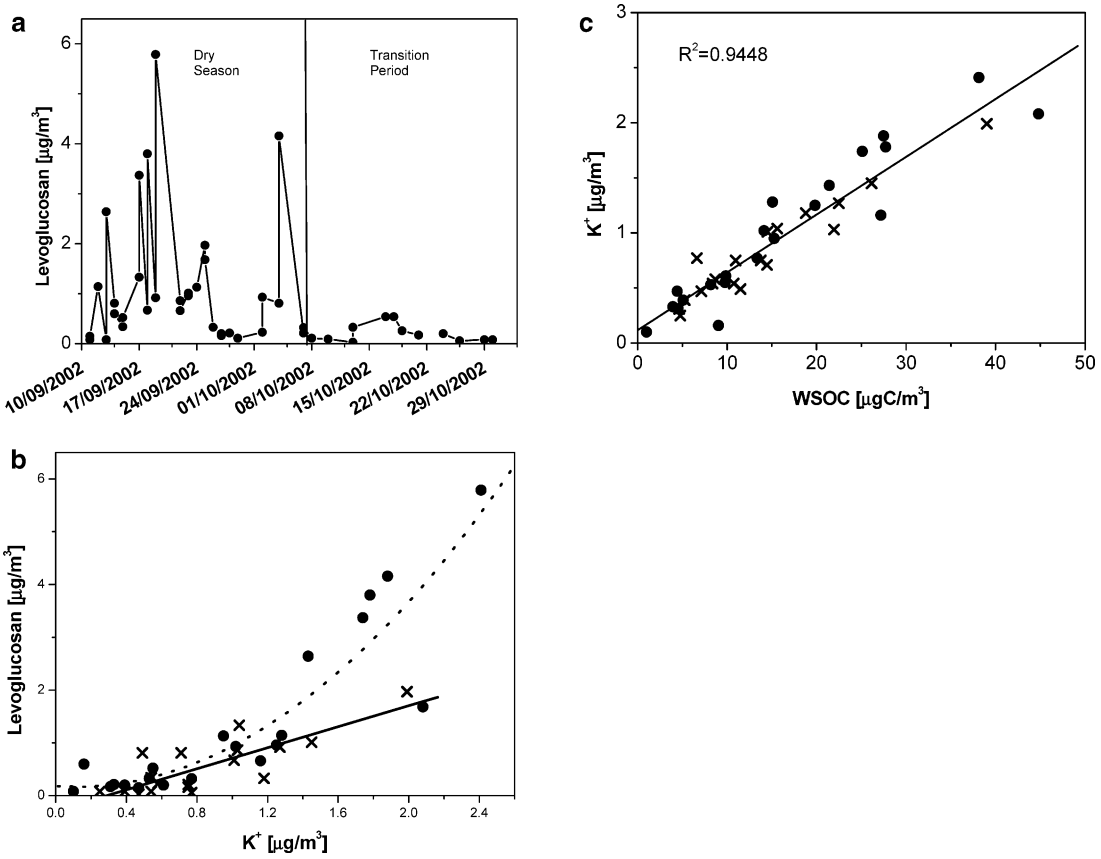

FIGURE 6. (a) Time series of levoglucosan concentrations in PM2.5 high-volume smoke samples collected during the LBA-SMOCC campaign. Note the difference between dry season samples (very smoky conditions) and transition-period samples. Wet season samples (cleaner conditions) are not shown since concentrations lie below detection limit. Uncertainty = 15%. (b) Comparison between levoglucosan and K^+ (*32*) values, daytime values in crosses and nighttime values in circles. A linear fit is shown for the daytime values (solid line, R^2 = 0.8065), and a polynomial fit (second degree) is shown for the nighttime values (dotted line, R^2 = 0.8234). This was done since levoglucosan correlation to K^+ varies diurnally: during night, there is more levoglucosan per K^+ than during day. (c) Comparison between K^+ and WSOC concentrations from a parallel sampler. K^+ correlates well with WSOC, without diurnal variation.

deforestation fires are set, flaming combustion prevails, while at nighttime, when the fire has subsided, smoldering processes are more dominant. A similar variation in the levoglucosan to K^+ ratio due to the stage of combustion (smoldering versus flaming) was reported by Gao et al. (*23*). Flaming combustion is a very exothermic gas-phase combustion, during which organic compounds are oxidized to a greater extent, thus leaving proportionally less levoglucosan. It has recently been reported that in 400 °C (as opposed to 250−300 °C) levoglucosan re-polymerizes into polysaccharides, which then further react to form organic solids containing conjugated double bonds and carbonyl groups (*33*), such as can be found in HULIS. Smoldering combustion, on the other hand, is a slow solid-phase oxidation process which gives rise to more unbroken organic compounds (*2*), and possibly to less levoglucosan re-polymarization, increasing the levoglucosan concentration in comparison to inorganic species such as K^+. This is supported by higher HULIS concentrations during daytime versus nighttime, reported in further SMOCC-campaign papers (*34*, *35*).

In Table 2, the percentage of WSOC, which levoglucosan accounts for, is shown. WSOC was determined for R1HiVo samples by the UGent team. For determination method, please refer to Chi and Maenhaut (*36*). The ratio ranges between <LOD and 7.1% with an average of 2.5%. However, there is a diurnal variation in this parameter as well: levoglucosan carbon accounts for <LOD−4.0% (average = 1.4%) of WSOC during daytime, and for 0.9−7.1% (average = 3.3%) of WSOC during nighttime. In Figure 6c, a correlation between K^+ and WSOC values is shown. It can be seen that they correlate well (R^2 = 0.9448) exhibiting no diurnal variation. PM2 (particulate matter < 2 μm) values were determined gravimetrically by the UGent team for samples collected in parallel (*36*), and it was found that both WSOC and K^+ correlate well with PM values as well (R^2 = 0.9747, 0.9672, accordingly). For K^+ and PM concentrations, see Table 2.

Size-Segregated Samples. Size-segregated smoke samples were collected by the Institute of Physics, University of São Paulo, São Paulo, Brazil, using a MOUDI impactor. These samples were analyzed using the new method. Size distributions of levoglucosan, 2-methylerythritol, particulate matter (PM), and K^+ for three samples collected during the dry (a and b) and transition (c) periods are shown in Figure 7. As can be seen in the figures, levoglucosan is most abundant in particle size bins between 175 nm and 1 μm, which is the fine fraction typical of smoke. This is also true for PM and for K^+, indicating that levoglucosan is a primary combustion product (*32*).

The size distribution of 2-methylerythritol is similar to that of levoglucosan (Figure 7a and b). In a recent work, Claeys et al. suggest that 2-methyltetrols are formed through isoprene oxidation by hydrogen peroxides (*21*). Lee et al. (*37*) found that hydrogen peroxide is emitted directly from biomass burning. As isoprene is abundant in the forest atmosphere, it is possible that 2-methyltetrols are formed from isoprene oxidation by hydrogen peroxide emitted from the fires. In the transition-period sample (Figure 7c), 2-methylerythritol distribution shows an additional peak (at

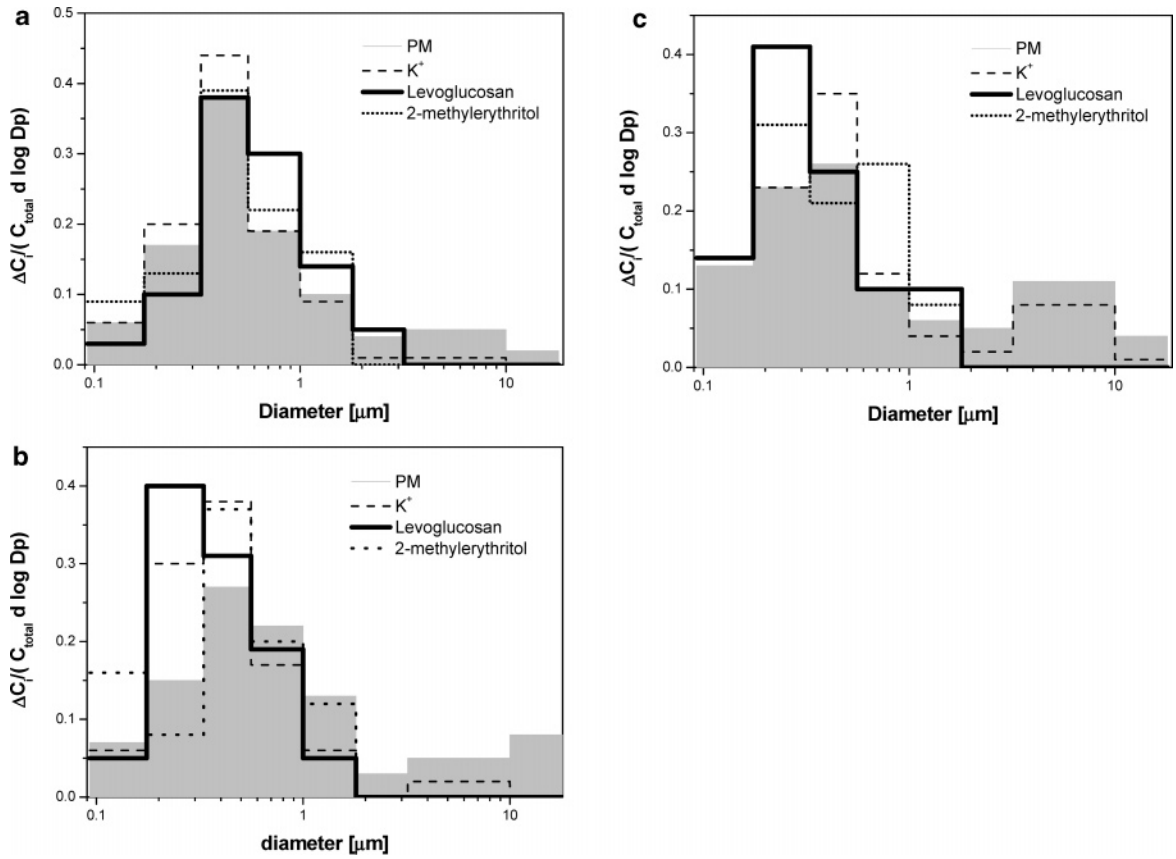

FIGURE 7. Normalized size distributions of levoglucosan (solid line), 2-methylerythritol (dotted line), K^+ (dashed line), and particulate matter (gray area) in size-segregated smoke samples collected in Rondônia, Brazil, during the SMOCC campaign. Sampling dates: (a) September 23, 2002 (dry season, smoky conditions); (b) October 3−5, 2002 (dry season, smoky conditions); and (c) October 17−18, 2002 (transition period, semiclean conditions). Where levoglucosan and 2-methylerythritol do not appear, they are below detection limit. In most stages, the uncertainty is 15%. In certain stages, levoglucosan concentration was under LOQ, and thus its uncertainty is 23% in these stages: (a) 0.093 and 1.8 μm; (b) 0.093 and 1 μm; and (c) all except 0.175 μm.

0.56−1 μm) to the one it shares with levoglucosan, suggesting that when biomass burning activities are scarce, other processes leading to 2-methyltetrols formation become important.

Unlike levoglucosan, K^+ appears also in the coarse mode, indicating a source other than vegetation combustion (In Figure 7b and c). According to elemental data obtained for parallel samples by the UGent team, the crustal enrichment factor $(=(K/Al)_{aerosol}/(K/Al)_{crust})$, relative to the average crustal rock composition of Mason and Moore (*38*), was about 2.3 in the coarse size fraction for the samples of Figure 7b and c. This indicates that the additional source is of crustal and primary biogenic origin, as was also observed previously in this region (*39*).

Arabitol, a saccharidic compound related to primary biogenic emissions (*14*), was detected and confirmed by spiking in some MOUDI samples and in an extract of *Penicillium aurantiogriseum* fungal spores. The absorption spectra of the arabitol peak in the MOUDI and fungal spores samples were compared and found to be very similar, possibly indicating a fungal spores source in some of the samples. The fungal spores samples contained K^+ in significant concentrations, suggesting a possible source for non-combustion-related K^+ in MOUDI samples.

The results from size-segregated sample analysis support levoglucosan's superiority as a specific biomass burning marker in comparison to K^+, which has contributions from other sources (such as crustal and biogenic emissions) as well. However, on the basis of the correlations from high-volume samples, it is suggested that while levoglucosan is indeed a more specific tracer, the levels of PM or WSOC emitted in the smoke cannot be directly estimated from its concentrations, due to the diurnal variation in the levoglucosan/WSOC and levoglucosan/PM ratios. However, once determined, on the basis of the presence of levoglucosan, that the source of the particles in a certain sample is indeed biomass burning, it may be possible to estimate PM or WSOC concentrations from the sample's K^+ values, since K^+ correlates with those species without diurnal variation. To do this, it is necessary to conduct a combined chemical analysis of the samples, quantifying both levoglucosan and other, ionic, species. Such an analysis is possible using the new method reported here.

Rainwater Analysis. Rainwater samples collected by the Institute of Physics, University of São Paulo, São Paulo, Brazil, were analyzed using the newly developed method. Since rainwater samples are often too dilute for analysis, we have concentrated them to the smallest volume that could be used. Levoglucosan concentrations detected in those samples ranged from 0.4 to 1.5 μg/mL. These values should be considered as qualitative only, since sample evaporation during shipment is suspected. The presence of levoglucosan in the samples suggests either in-cloud processes such as droplet nucleation on smoke particles or mixing of smoke particles and cloud droplets, which have both been shown to lead to substantial effects on cloud microphysics and climate (*10*). Smoke could have also been scavenged by rain. Analysis of levoglucosan in the rainwater using the GC/MS method is more difficult due to the need to keep very dry conditions.

Acknowledgments

We thank Prof. M. Claeys from the Department of Pharmaceutical Sciences, University of Antwerp, Antwerp, Belgium, for providing data for comparison and for very useful comments. This work is a contribution to the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). We are indebted to the European Commission, Project SMOCC (Contract EVK2-CT-2001-00110), the Belgian Federal Science Policy Office, the "Fonds voor Wetenschappelijk Onderzoek − Vlaanderen", and the FAPESP and CNPq, Brazil, for research support. Y.R. acknowledges support from the RPH-Promotor Stiftung in memory of Ernst and Anni Deutsch, the Dr. Angel Faivovich Foundation, and the Sussman Family Center for the Study of Environmental Sciences. We thank Alcides Camargo Ribeiro, Ana Lucia Loureiro, Tarsis Germano, Gilberto Nishioka, and Jan Cafmeyer for collecting the samples at the field site and Svetlana Katsman for IC analysis of numerous samples.

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Received for review October 20, 2004. Revised manuscript received January 20, 2005. Accepted January 26, 2005.

ES048363C