**Determination of Sugar Compounds in Atmospheric Aerosols by Liquid
Chromatography Combined with Positive Electrospray Ionization Mass Spectrometry**

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Abstract

We here report a method for the determination of sugar compounds of known presence in atmospheric aerosols using liquid chromatography (LC) combined with positive electrospray ionization mass spectrometry (MS). The target analytes include C₃-C₆ monosaccharide alcohols (glycerol, erythritol, xylitol, mannitol), C₃-C₆ monosaccharides (xylose, glucose, and levoglucosan), a disaccharide (sucrose), and a trisaccharide (melezitose). A mobile phase consisting of 20% 10 mM aqueous ammonium acetate, 8% methanol, and 72% water was found to provide abundant $[M+NH_4]^+$ adduct ions when coupled with electrospray ionization. Use of a polymer-based amino analytical column resolved the target compounds from the bulk solvent and provided limited separation among the target compounds. The target analytes were quantified using their $[M+NH_4]^+$ ions. Sample pretreatment was greatly simplified in comparison with the more commonly used gas chromatographic methods. It involved extraction of aerosol filters in methanol, evaporation of the solvent, and reconstitution with 5 mM ammonium acetate in water prior to the LC-MS analysis. The analyte recoveries were measured at the levels of 100, 500 and 1000 $\mu\text{g/L}$ to be in the range of 78 – 102%, 94 – 112%, and 92 – 110%, respectively. The detection limits were lower than 10 pmol/injection for the tested target compounds except for xylose. Xylose had a detection limit of 95 pmol/injection. The method was applied to analyze 30 atmospheric aerosol samples to demonstrate its feasibility. The LC-MS method made possible the detection of trisaccharides as aerosol constituents for the first time.

Keywords: LC-MS analysis of aerosol organics; Levoglucosan; disacchrides; trisacchrides; sugar alcohols

1. Introduction

Organic carbon (OC) accounts for a significant fraction of fine aerosol mass, typically ranging from ~10% in the rural atmosphere to ~30% in the urban environment (1). Chemical characterization of the OC fraction at a molecular level has mainly focused during the past
5 few decades on the organic-solvent extractable portion that is amenable to gas chromatography-mass spectrometry (GC-MS) analysis (e.g., 2-4). These relatively non-polar compounds only accounted for 10-30% of OC mass (3, 5, 6). Recent studies have indicated that water-soluble organic compounds can be a dominant fraction of OC, especially in rural and remote atmospheres (e.g., 7). Despite the abundance of water-soluble organic carbon
10 (WSOC) in atmospheric aerosols, its molecular composition is less studied due to the diverse nature of its constituents (8), which require diverse analytical techniques for their determination. A number of sugar compounds, such as levoglucosan, glucose, glycerol, and sucrose, are known to be present in atmospheric aerosols as a result of biomass combustion and soil resuspension (e.g., 6, 9-13). The analysis of these sugar compounds is important for
15 aerosol source apportioning (e.g., 5, 14) and understanding of the impact of biomass burning aerosols on local and regional air quality as well as on the global climate.

The existing analytical methods for sugar compounds fall into four categories, GC-based methods, high performance liquid chromatography (HPLC)-based methods, direct MS methods, and LC-MS methods (15). The GC-based methods require derivatization of the
20 hydroxyl groups. The most-used derivatization technique is silylation using bis(trimethylsilyl)trifluoroacetamide (BSTFA), which causes multiple derivatives for sugar compounds with both aldehyde and -OH groups as a result of unwanted silylation of the aldehyde group (9). The derivatization step also adds extra sample handling and chemical manipulation, therefore becoming more labor-intensive and prone to contamination. The
25 HPLC methods utilize a suitable column for separation and a variety of detection methods, including electrochemical detection (16), refractive index (RI) detection, evaporative light-

scattering detection (ELSD) (17). In general, sugar compounds lack chromophoric and fluorophoric moieties required for UV and fluorescence detection. As a result, less sensitive HPLC detection methods such as RI and ELSD are used. These detection methods typically provide detection limits in the range of 0.05 -1.2 $\mu\text{g}/\text{injection}$ (18), rendering them not practical for measuring the trace levels in atmospheric aerosols. The direct MS methods inject the sample extracts into a LC-MS system with the LC column removed (11). The coexistence of sample matrix components could adversely affect sensitivity in the direct MS methods (19, 20). An LC-MS method in the negative ion mode was reported by Niwa et al. (21) for monosaccharides and polyols in uremic serum samples. The application of LC-MS to study sugar compounds in atmospheric aerosols is so far very limited. The study by Dye and Yttri (22) was the only study we found in the literature that reported an LC-MS method for the determination of three monosaccharide anhydrides in atmospheric aerosols.

In this work, we present an LC-MS method for the determination of the atmospherically relevant sugar compounds and demonstrate its use with real aerosol samples. Figure 1 shows the chemical structures of nine target analytes selected for this study. With the exception of melezitose, the presence of other sugar compounds has been reported in ambient aerosols or biomass burning aerosols (e.g., 6, 9, 11-13, 23). The detection of any trisaccharides in atmospheric aerosols has not been reported in the literature. This may well be due to the inability of GC based methods for their detection. Melezitose is included as a trisaccharide example in our list of target compounds to check their presence since our LC-MS method does not have the limitations of the previous GC methods.

2. Experimental

2.1 Reagents and standards

All the organic solvents were LC grade. UV-irradiation treated high purity water (18 M Ω , supplied by a Milli-Q water-purification system, Millipore, Bedford, MA, USA) was

used wherever water was needed. The sugar standards were from Acros Organics (Geel, Belgium) and used as purchased without further purification. Ammonium acetate (NH₄Ac) of analytical grade was purchased from BDH (Poole, UK). Levoglucosan-¹³C isotope was purchased from Cambridge Isotope (Andover, MA, USA) and used as an internal standard (IS). Individual standard stocks were made at the level of 500 mg/L in water and subsequently used to make a composite standard of 4.00 mg/L. The individual and the composite standard solutions were stored at 4°C and tested to be stable for at least three months. The composite standard was further diluted using water to prepare calibration standards ranging from 60 to 1000 µg/L.

2.2 Aerosol sample collection and pre-analysis treatment

Atmospheric particulate matter of less than 2.5 µm (PM_{2.5}) was collected over 24-hr periods onto filters at a flow rate of 1.13 m³/min using a high-volume sampler (GT22001; Andersen Instruments, Smyrna, GA, USA). The collection substrates were 20×25 cm quartz fiber filters (Pall Gelman, Ann Arbor, MI, USA), prebaked overnight at 550°C to remove any adsorbed organic materials. The aerosol samples were collected over the period of August 2004 – April 2005 on the campus of the Hong Kong University of Science and Technology. After collection, the filter samples were stored in prebaked aluminum foil at 4°C until analysis. Ten 1×1.45 cm² sized pieces were removed from each filter using a stainless steel filter punch and transferred to an Erlenmeyer flask. The filter samples were then spiked with 31.2 ng levoglucosan-¹³C in an aliquot of 50 µL solution, followed by extraction with two portions of 2.5 mL methanol in an ice ultrasonic bath for 10 minutes. The extract was filtered through a 5 µm Teflon filter, transferred to a 15 mL screw cap centrifuge tube, and evaporated to dryness at 40°C under a gentle nitrogen stream. The residue was reconstituted with a 250 µL aqueous solution of 5 mM ammonium acetate and thoroughly vortex-mixed for 30 seconds. The samples were analyzed within 30 days.

2.3 LC-MS analysis

The samples or the standard solutions were injected into an LC-MS system for quantification. The LC-MS system consisted of a Waters 2695 HPLC and a Waters ZQ micromass quadruple MS, equipped with an electrospray ionization (ESI) source and a nitrogen solvent sparging unit. An injection volume of 100 μ L was used. The column for separation was a Prevail carbohydrate ES column (250 $\times$ 4.6 mm) packed with 5 μ m spherical polymer beads coated with amino-based proprietary bonding material (Alltech, Deerfield, IL, USA). Isocratic elution was carried out in a mobile phase consisting of 20% 10 mM NH_4Ac , 8% methanol and 72% water. The column was kept at a temperature of $25 \pm 1^\circ\text{C}$. The flow rate was 0.3 mL/min, and the total flow from the column was directed to the ESI source. After LC separation, the analytes were determined by electrospray ionization mass spectrometry (ESI-MS) operated in the positive ion mode. The $[\text{M}+\text{NH}_4]^+$ ions were found to be abundant and therefore selected for monitoring and quantification. Table 1 tabulates the m/z values of the $[\text{M}+\text{NH}_4]^+$ ions for individual analytes. Calibration curves were established by plotting peak area ratios of the $[\text{M}+\text{NH}_4]^+$ ions between the analytes and the IS versus the analyte concentrations. The calibration slopes, intercepts, and coefficient of determination for the sugar standards are listed in Table 1.

3. Results and discussion

3.1 Ionization and MS conditions

Sugar compounds, as a group of molecules containing multiple hydroxyl functional groups, are not easily protonated to form $[\text{M}+\text{H}]^+$ ions in the positive ESI mode. Ionization efficiency could be improved by forming adduct ions with inorganic cations. Three cations, Na^+ , Pb^{2+} , and NH_4^+ , could form complexes with hydroxyl groups, and were tested for their ability in promoting ionization. The use of sodium or lead ions was demonstrated by Salpin and Tortajada (24). We tested the feasibility of using Pb^{2+} and found that, depending on the Pb^{2+} concentration, one or more Pb^{2+} ions could attach to one sugar molecule. Formation of

the multiple adduct ions in effect reduces detection sensitivity of a chosen monitoring ion. Consequently, Pb^{2+} was not pursued further.

For the purpose of identifying abundant ions that are characteristic of the target analytes, we first studied MS fragmentation patterns by directly infusing single compound standards at a level of 1.0 mg/L into the ESI source at a flow rate of 20 $\mu\text{L}/\text{min}$. The standards were dissolved either in 5 mM NH_4Ac or 5 mM NaCl aqueous solutions. The adduct ions, $[\text{M}+\text{Na}]^+$ and $[\text{M}+\text{NH}_4]^+$, were found to be dominant in their respective ESI mass spectra. Figure 2 shows the ESI-MS of eight target analytes in the presence of NH_4Ac . Although the $[\text{M}+\text{NH}_4]^+$ ions were not always the most abundant ion, they were invariably abundant in the ESI-MS of all the tested sugar standards. The $[\text{M}+\text{H}]^+$ ions were observed in the ESI-MS of glycerol, erythritol, xylitol, manitol, and sucrose, but were absent in the ESI-MS of glucose, levoglucosan and melezitose (Figure 2). In the presence of NaCl , the $[\text{M}+\text{Na}]^+$ ions were always the most abundant ions in the ESI-MS (not shown). When analyzing 1.0 mg/L individual standards, we found peak areas of the $[\text{M}+\text{Na}]^+$ ions to be less than one-quarter of those of the $[\text{M}+\text{NH}_4]^+$ ions for glucose, xylitol, and levoglucosan and slightly larger than one for mannitol. Either Na^+ or Pb^{2+} , as a nonvolatile salt, deposits around the interface of the LC-MS, causing elevation of the background signal and therefore making frequent desalting maintenance necessary. In comparison, NH_4^+ compounds had the advantage of being volatile and requiring less ESI source cleaning. For these reasons, analysis using $[\text{M}+\text{Na}]^+$ ions was not further pursued.

During method development, the tuning parameters for the ESI source were varied to obtain the maximum $[\text{M}+\text{NH}_4]^+$ ion intensity for individual compounds. The resulting individual tune files were found to be not dramatically different from one another. The following tuning parameters were found to be optimal for the suite of target sugar compounds: capillary voltage, 3.0 kV; cone voltage, 10 V; extractor voltage, 2 V; RF lens, 0.3 V; source

temperature, 110°C; desolvation temperature, 450°C; desolvation gas flow, 600 L/hr; cone gas flow, 50 L/hr.

The overall ionization efficiency to form $[M+NH_4]^+$ ions on a per sugar molecular basis peaked at C₆ sugar. This can be seen from the slope values of the calibration curves, which plot the IS-normalized peak areas versus the concentrations of the sugar standards in μ M. The ionization efficiency declined when the carbon number is either increased or lowered from C₆. The C₅ sugar, xylose, was an exception. It had the lowest ionization efficiency among all the tested sugar compounds.

3.2 Optimization of chromatographic conditions

Optimization of chromatographic conditions cannot be made independently from that of the MS component (25). When one considers the trace level nature of the analytes present in the aerosol samples and the co-existence of hundreds of other compounds, some degree of separation is desired before ionization and MS detection to minimize signal suppression and other interferences from the bulk matrix of the sample. A C₁₈ (octadecyl) reversed phase column was first tried for separation. Being strongly hydrophilic, the target sugar compounds showed no retention on the C₁₈ column when eluting by a mobile phase consisting of NH₄Ac and methanol. A normal phase column is expected to be able to separate these highly polar target compounds.

The Alltech Prevail carbohydrate column was tested and found to have sufficient retention of carbohydrates. The LC system had a dead time of 5.2 min. In comparison, all the analytes had a retention time of greater than 8 min, therefore ensuring complete separation from the bulk solvent of the sample. Two organic solvents, methanol and acetonitrile, were tested. The intensity of the $[M+NH_4]^+$ ions first increased with increased amounts of methanol, peaked at 8-9% of methanol, and decreased at 10% methanol (Figure 3a). The concentration of acetonitrile had slightly different effects on the yield of $[M+NH_4]^+$ ions. The intensity of the $[M+NH_4]^+$ ions first decreased with an increasing percentage of acetonitrile,

followed by an increase with an increasing percentage of acetonitrile. The $[M+NH_4]^+$ ion then peaked at 6% of acetonitrile (Figure 3b). The maximum signals using methanol were 30-600% higher than those using acetonitrile. As a result, methanol was selected as the organic modifier for later experiments and the percentage of methanol was fixed at 8%. Under this elution condition, the retention time separation among the analytes was limited, ranging from none (i.e., xylitol and sucrose) to 0.53 min (i.e., xylose and levoglucosan) among the neighboring analytes. Table 1 lists the retention times of the target analytes.

A good separation of monomeric sugar compounds on the carbohydrate LC column typically required a mobile phase of acetonitrile and water with more than 70% of acetonitrile (26). However, Figure 3 clearly shows that the MS detection sensitivity diminished when the percentage of organic solvent increased to higher than 10%. Apparently, a good separation and acceptable MS sensitivity could not be achieved at the same time. Fortunately, due to the high specificity of MS detection, a baseline separation of the analytes is not necessary. Figure 4 shows the LC chromatograms of individual monitoring ions in an ambient aerosol sample. It demonstrates that the specificity of MS eliminates the need for complete separation of the individual compounds of different molecular weight. The retention times were found to be extremely stable, varying within ± 0.02 min. As a result, the retention times are still useful for verifying the presence/absence of analytes of different molecular weight.

The lack of separation among sugar compounds does pose one limitation. That is, sugar compounds of identical molecular weights (e.g., glucose, fructose) can not be differentiated.

3.3 Method recoveries, precision, and limits of detection

We evaluated the extraction efficiency and reproducibility of the analytical procedure by analyzing six replicates of blank filter samples doped with mixtures of the sugar standards at three different concentrations (i.e., 100, 500, and 1000 $\mu\text{g/L}$). The extraction efficiencies of the analytes were determined by comparing the peak areas of the spiked samples with

those of the corresponding liquid standards. The results are summarized in Table 2. At the highest concentration level of 1000 $\mu\text{g/L}$, the recoveries varied from 92% to 110% among the individual analytes. At the two lower concentration levels, the recovery ranges were 94-112% at 500 $\mu\text{g/L}$ and 78-102% at 100 $\mu\text{g/L}$. The reproducibility of the analytical procedure can be evaluated through the relative standard deviation (RSD) of the replicate measurements. The RSD values ranged from 5% to 26%, generally higher RSD values at the lower concentration levels. These values demonstrated satisfactory extraction efficiencies irrespective of the analyte levels and reasonable reproducibility of the analytical method.

The limit of detection (LOD) was calculated as the concentration that corresponds to three times the standard deviation of the peak areas generated by filter samples spiked with 20 $\mu\text{g/L}$ of the sugar standards. The LODs varied from 1.0 to 9.1 pmol/injection for the target sugar compounds with the exception of xylose (Table 1). Due to its lower ionization efficiency, xylose had an LOD of 95 pmol/injection, an order of magnitude higher than other compounds. The LOD of levoglucosan by our LC-MS method is comparable to that by the GC-MS method (0.62 pmol/injection) (23). The LODs for other compounds by the GC-MS methods are not available for comparison. If we assume a sampled air volume of 1622 m^3 (24 hr sampling at the designated flow rate of 1.13 m^3/min for the high-volume sampler) and that 3.4% of the filter is used for analysis, these LODs translate to air concentrations of 0.65 ng/m^3 for xylose and 0.009-0.208 ng/m^3 for other compounds.

3.4 Analysis of aerosol samples

We used the method to quantify the target sugar compounds in 30 atmospheric aerosol samples. All nine target sugar compounds were found in the samples. Figure 4 shows typical SIM chromatograms of the target analytes in one aerosol sample. Table 3 reports the means and the ranges of the concentrations of these compounds. The sum of the sugar compounds ranged from 39 to 1310 ng/m^3 . Trisaccharides were detected in 12 out of the 30 ambient samples. The average abundance of trisaccharides was about one-third the

abundance of disaccharides. Levoglucosan was the most abundant sugar species, on average accounting for 35% of the detected sugar compound mass. The average concentration of levoglucosan was 1.2–24.2 times the concentrations of other target sugar compounds. The sample collected on 19 October 2004 showed the highest concentrations of all the target
5 analytes among the thirty aerosol samples. Three hill fires in the region were reported by the news media to have erupted in the three-day prior to 19 October 2004. The first fire burned an area of more than one-tenth km² in a place 150 km northwest to Hong Kong on 16 October. The second fire burned three hills also approximately 150 km northwest to Hong Kong on the night of 17 October. The third fire burned an area of ~2000 m² about 25 km north to Hong
10 Kong. Our chemical analysis results verified the presence of biomass burning.

The correlation matrix of the target sugar compounds (Table 4) reveals moderate to strong correlations ($0.461 < r < 0.953$) among the primary saccharides (e.g., glucose, sucrose) and saccharide polyols (e.g., erythritol, manitol). The highest correlation ($r = 0.953$) was found between sucrose and melezitose. The good correlations suggest that these compounds
15 shared common dominant sources. The correlations of levoglucosan, an anhydrosaccharide species, with other sugar compounds were weaker ($0.415 < r < 0.674$), although still significant.

4. Conclusion

20 An LC-MS method was developed for the determination of nine sugar compounds present in atmospheric aerosols. In comparison with the more commonly used GC-MS methods, the LC-MS method greatly reduces sample pretreatment by eliminating the need for derivatization. The LC-MS method also makes it possible to analyze trisaccharides, while the GC/MS methods do not have this capability. Recoveries for those target compounds were in
25 the range of 78–112%. Detection limits of <10 pmol/injection were achieved for all test sugar compounds except for xylose. In the ambient sample analysis, the most abundant sugar

compound was levoglucosan. This application demonstrates the usefulness of such a LC-MS method for sugar compounds in the study of atmospheric organic particulate matter.

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Table 1. Molecular weights, MS quantification ions, calibration curve parameters, and limits of detection of the target sugar compounds

Compounds	Compound Class	MW	[M+NH ₄] ⁺	RT (min)	Concentration ^a range (μM)	Slope (uM)	Intercept (uM)	r ²	LOD ^b	
									pmol/injection	pmol/m ³
Glycerol	C ₃ sugar alcohol	92	110	9.05	0.65-10	0.239	0.274	0.998	8.4	0.38
Erythritol	C ₄ sugar alcohol	122	140	8.88	0.50-8.2	0.457	0.958	0.990	2.1	0.09
Xylitol	C ₅ sugar alcohol	152	170	8.76	0.40-6.6	0.796	1.260	0.990	4.7	0.21
Mannitol	C ₆ sugar alcohol	182	200	8.82	0.30-5.5	0.865	1.044	0.991	1.0	0.05
Xylose	C ₅ sugar	150	168	9.17	0.40-6.7	0.209	0.514	0.987	95	4.32
Glucose	C ₆ sugar	180	198	8.99	0.30-5.6	0.804	1.843	0.980	1.2	0.05
Levoglucozan	C ₆ anhydrosugar	162	180	9.70	0.35-6.2	0.726	0.619	0.997	1.4	0.07
Sucrose	Disaccharide (C ₁₂)	342	360	8.76	0.18-2.9	0.566	0.192	0.997	7.9	0.36
Melezitose	Trisaccharide (C ₁₈)	504	522	8.41	0.12-2.0	0.510	0.110	0.998	9.1	0.41

^a The concentration ranges correspond to a uniform range of 60-1000 μg/L for the individual standards.

^b LODs in pmol/injection were based on an injection volume of 100 μL; LODs in pmol/m³ were based on a sample volume of 1622 m³ and 3.4% of the high volume filter used for analysis.

Table 2. Recoveries of the target sugar compounds

Compounds	Spiked conc. ($\mu\text{g/L}$)	Measured conc. ($\mu\text{g/L}$)	R.S.D. (%) (n = 6)	Recovery (%)
Mannitol	99.7	95 ± 15	16	95 ± 15
	498	558 ± 41	7	112 ± 8
	997	1088 ± 55	5	109 ± 5
Glucose	100	90 ± 19	21	90 ± 19
	502	608 ± 37	6	105 ± 6
	1003	1106 ± 82	7	105 ± 8
Levogluconan	112	92 ± 19	21	82 ± 17
	561	599 ± 89	15	107 ± 16
	1122	1046 ± 89	9	93 ± 8
Xylitol	104	81 ± 16	19	78 ± 15
	518	546 ± 39	7	105 ± 8
	1037	1145 ± 60	5	110 ± 6
Erythritol	100	101 ± 20	20	93 ± 18
	502	603 ± 80	13	111 ± 15
	1004	1179 ± 198	17	109 ± 18
Glycerol	108	99 ± 16	16	92 ± 15
	542	361 ± 94	26	97 ± 17
	1084	1077 ± 124	11	99 ± 11
Xylose	112	112 ± 12	11	100 ± 10
	491	513 ± 17	3	104 ± 3
	1116	1030 ± 41	4	92 ± 4
Sucrose	116	104 ± 6	6	89 ± 6
	511	479 ± 50	10	94 ± 8
	1161	1101 ± 34	3	95 ± 3
Melezitose	102	104 ± 6	6	102 ± 6
	448	473 ± 17	4	106 ± 4
	1018	1017 ± 33	3	100 ± 3

Table 3. Means and ranges of concentrations of the target sugar compounds detected in aerosol samples

Compound	air concentrations (ng/m ³)	
	Mean ^b	Range ^c
Glycerol	10.39	0.7-61.2
Erythritol	5.35	1.0-28.2
Xylitol	6.10	0.9-21.4
Mannitol	3.62	nd-16.6
C5 sugars (xylose) ^a	71.97	0.7-474.8
C6 sugars (glucose) ^a	17.96	3.2-84.4
Levogluconan ^a	87.68	4.1-269.8
Disaccharides (sucrose) ^a	17.25	nd-202.5
Trisaccharides (melezitose) ^a	6.22	nd-62.3
sum	226.5	39.0-1309.6

^a The compound inside parenthesis was used as the calibration standard for the respective group of sugar isomers of identical molecular weights.

^b $n = 30$.

^c nd refers to not-detected.

Table 4. Correlation (r) matrix of the aerosol concentrations of the nine sugar compounds

	Glycerol	Erythritol	Xylitol	Mannitol	C5 sugars (xylose)	C6 sugars (glucose)	Levogluconan	Disaccharides (sucrose)	Trisaccharides (melezitose)
Glycerol	1								
Erythritol	0.768	1							
Xylitol	0.577	0.709	1						
Mannitol	0.461	0.735	0.385	1					
C5 sugars (xylose)	0.680	0.848	0.632	0.721	1				
C6 sugars (glucose)	0.759	0.935	0.712	0.721	0.790	1			
Levogluconan	0.415	0.646	0.517	0.674	0.486	0.665	1		
Disaccharides (sucrose)	0.732	0.870	0.666	0.622	0.825	0.852	0.496	1	
Trisaccharides (melezitose)	0.669	0.820	0.675	0.618	0.764	0.833	0.528	0.953	1

Note: (1) Values in bold (except diagonal) are significant at the level of significance $\alpha=0.050$ (two-tailed test).

(2) The compounds inside parentheses were used as the calibration standards for the respective groups of sugar isomers of identical molecular weights.

Figure captions

Figure 1. Structures of the target sugar analytes.

Figure 2. Background subtracted mass spectra of the target sugar compounds.

Figure 3. Peak areas of $[M+NH_4]^+$ ions versus different compositions of methanol (a) and acetonitrile (b) in mobile phase. (The percentage of 10 mM ammonium acetate in the mobile phase was fixed to be 20%. The rest of the mobile phase is water.)

Figure 4. SIM chromatograms of an aerosol sample.

(Note levoglucosan is scaled by a factor of 0.3.)

Figure 1. Structures of the target sugar analytes

Figure 2. Background subtracted mass spectra of the target sugar compounds.

Figure 3. Peak areas of $[M+NH_4]^+$ ions versus different compositions of methanol (a) and acetonitrile (b) in mobile phase. (The percentage of 10 mM ammonium acetate in the mobile phase was fixed to be 20%. The rest of the mobile phase is water.)

Figure 4. SIM chromatograms of an aerosol sample.

(Note levoglucosan is scaled by a factor of 0.3.)