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Technical note

A highly resolved anion-exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol

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ABSTRACT

An improved high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) method is developed and validated for simultaneous determination of atmospherically relevant sugar alcohols, monosaccharides, and monosaccharide anhydrides. The improved method enables the separation of levoglucosan and arabitol which were not or insufficiently separated by the previous HPAEC–PAD methods. Reproducibility of the method was tested for both standard solutions and atmospheric aerosol samples. The peak area relative standard deviation (RSD%) of standard solutions were found to be lower than 1.5% for consecutive analyses ($n=3$) and lower than 4% for day to day variation ($n=9$). The peak area RSD% of atmospheric samples with typical European wintertime monosaccharide concentrations ($n=9$) was found to be similar to that of standard solutions. Limits of detection ranged from 0.002 mg L^{-1} for inositol to 0.08 mg L^{-1} for fructose. The developed method offers a simple, reliable and cost effective determination of atmospheric tracers for biomass combustion and for selected bio-aerosol components at sub-nanogram per cubic-meter-air concentration levels for routine analysis.

1. Introduction

Sugar alcohols, monosaccharides and monosaccharide anhydrides comprise an important fraction of water soluble organic carbon (WSOC) in atmospheric aerosols (Feng et al., 2007; Fine et al., 2004; Gelencsér et al., 2007; Gorin et al., 2006; Krivacsy et al., 2006; Lukács et al., 2007; Puxbaum et al., 2007; Simoneit et al., 2004; Yttri et al., 2007). Levoglucosan, mannosan and galactosan, which originate from combustion of cellulose and hemicellulose, typically comprise a large fraction of saccharidic compounds in atmospheric aerosols during winter months due to residential wood burning (Pashynska et al., 2002; Puxbaum et al., 2007; Saarikoski et al., 2008) or from wildfires (Gao et al., 2003; Engling et al., 2006a; Mayol-Bracero et al., 2002; Puxbaum et al., 2007). During summer months, higher concentrations of primary biological sugar alcohols and monosaccharides such as inositol, arabitol, mannitol, glucose and fructose are typically observed (Bauer et al., 2008; Caseiro et al., 2007; Pashynska et al., 2002). The reported concentrations of levoglucosan in atmospheric aerosols vary dramatically ranging from lower ng m^{-3} levels at an oceanic background site (Simoneit et al., 2004) to over 40 μg m^{-3} in wildfire smoke (Pashynska et al., 2002). The reported values for sugar alcohols and monosaccharides are less dramatic though their concentrations can vary by an order of magnitude from lower ng m^{-3} values to several hundred ng m^{-3} at an urban site (Pashynska et al., 2002).

Recently, high-performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC–PAD) methods for determination of atmospherically relevant saccharidic compounds were presented (Caseiro et al., 2007; Engling et al., 2006b). The methods are highly sensitive, selective to carbohydrates and require no complex sample pre-treatment procedures. In addition, the methods showed good agreements with derivatization GC/MS or GC/FID methods (Engling et al., 2006b; Caseiro et al., 2007) and an HPLC/ESI-MS method (Engling et al., 2006b). Although these studies demonstrated a potential merit of the HPAEC–PAD technique, the methods suffer from co-elution of levoglucosan and arabitol, which hinders a simple determination of these compounds in routine analysis.

In this work, we present an improved HPAEC–PAD method for the determination of eleven atmospherically relevant sugar alcohols, monosaccharides and monosaccharide anhydrides,

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such as those reported by Pashynska et al. (2002) and Caseiro et al. (2007). The new method is simple, selective, sensitive, quantitative, has a wide dynamic range and separates all eleven peaks of the compounds of interest well. The method is characterised for its limit of detection (LOD), reproducibility and quantification range using both standard compounds and atmospheric samples.

2. Experimental

2.1. Chemicals and standards

Ultra-pure (UP) water used in this study was prepared using a Milli-Q Gradient A10 with a UV lamp, with resistivity and TOC values of 18.2 MΩ cm^{-1} and 4 ppb, respectively (Millipore, Billerica, MA, USA). The chemicals, including *myo*-innositol (>99%), levoglucosan (>98%), D-(+)-arabitol (>99%), D-mannitol (>99%), D-(+)-mannose (>99%), D-(+)-glucose (99%), D-(+)-galactose (99%), D-(−)-fructose (99%) and sodium hydroxide solution (50% in H_2O, low carbonate ion chromatography grade) were obtained from Fluka (St. Louis, MO, USA). Mannosan (>98%) and galactosan (no quality stated) were obtained from Sigma (St. Louis, MO, USA) and *meso*-erythritol was obtained from Aldrich (St. Louis, MO, USA).

A stock solution containing eleven standard compounds was prepared in UP water (100 mg L^{-1}). The stock solution was diluted further by UP water to make a series of standard solutions at 0.02, 0.04, 0.08, 0.16, 0.31, 0.63, 1.25, 2.5, 5.0 and 10 mg L^{-1}. The stock solution was kept at −28 °C until needed for the preparation of standard solutions. The standard solutions (50 mL) were prepared freshly at the beginning of each analytical week and stored at 4 °C. A calibration was performed for each analytical sequence. No degradation of standard compounds was found during the course of the analytical week.

2.2. Instrumentation

The development and validation of the method were performed using a Dionex ICS-3000 system consisting of SP (quaternary pump and degasser), DC (column compartment), ED (electrochemical detector and gold electrode), EO (eluent organiser) units and an AS40 autosampler (Dionex, Sunnyvale, CA, USA). The waveform used for pulsed amperometric detection was the standard quadruple potential for carbohydrate analysis (Dionex Technical Note 21). The separation was carried out on a Dionex CarboPac MA1 column (4 × 250 mm) with a CarboPac MA1 guard column (4 × 50 mm) at room temperature. This column is suited for separation of reduced monosaccharides, enabling us to improve separation of previously unseparated or weakly separated monosaccharides using HPAEC–PAD methods. UP water (eluent A) and 1.0 M sodium hydroxide (eluent B) were used for the separation. The UP water was sparged with He for a minimum of 15 min to remove dissolved gases, particularly carbon dioxide. To prepare 1.0 M sodium hydroxide eluent, 104.6 mL of 50% (w/w) sodium hydroxide solution was diluted to 2 L. It is noted that the highest purity water and a low carbonate sodium hydroxide solution must be used for the preparation of eluents, as ionic impurities, especially borate and carbonate, disturb chromatographic separation. The eluent flow rate was 0.4 mL min^{-1}. The sample injection loop was 25 μL. All eluent reservoirs were blanketed by helium to minimise carbon dioxide contamination from the air. Instrumental controls, data acquisition, and chromatographic integration were performed using Dionex Chromeleon software.

2.3. Atmospheric sample collection

Atmospheric aerosol samples used for the method validation were collected on 6th October 2007, 25th December 2007 and 3rd February 2008 at the village of Seiffen, Saxony, Germany (50°38′50″ N, 13°27′08″ E, 647 m ASL). The village is known for its traditional wooden handcraft industry and is subject to significant influence of wood burning smoke during the winter months from both industrial and domestic wood combustion.

The samples were collected using a Digitel DHA-80 high volume sampler with a PM_{10} pre-separator (Digitel, Elektronik AG, Hegnau, Switzerland). The samples were collected for 24 h from midnight to midnight. The flow rate of the sampler was 30 m^3 h^{-1}. The samples were collected on pre-baked (105 °C, 24 h) quartz fibre filters (Munktell Filter AB, Falun, Sweden). No monosaccharides were found in the pre-baked filters or unexposed areas of field samples.

2.4. Sample preparation

A portion of each quartz fibre filter (6.28 cm^2) was extracted in 2.5 mL of UP water under ultrasonic agitation for 30 min. The extract was filtered through a syringe filter (0.45 μm, Ion Chromatography Acrodisc, Pall, NY, USA) to remove insoluble materials. The extraction efficiencies of the eleven standard compounds were determined by spiking a small volume of stock solutions onto blank filters. The spiked filters were dried and extracted in the same manner as the samples, resulting in extract concentrations of 1.25 mg L^{-1}. The extraction efficiencies were found to be in the range of 96% (mannosan) to 103% (fructose), similar to the extraction efficiencies reported for the previous HPAEC–PAD methods, using similar extraction procedures.

3. Results and discussion

3.1. Selection of eluent NaOH concentration for separation of levoglucosan and arabitol

The disadvantage of previously described HPAEC–PAD methods was the difficulty associated with the separation of

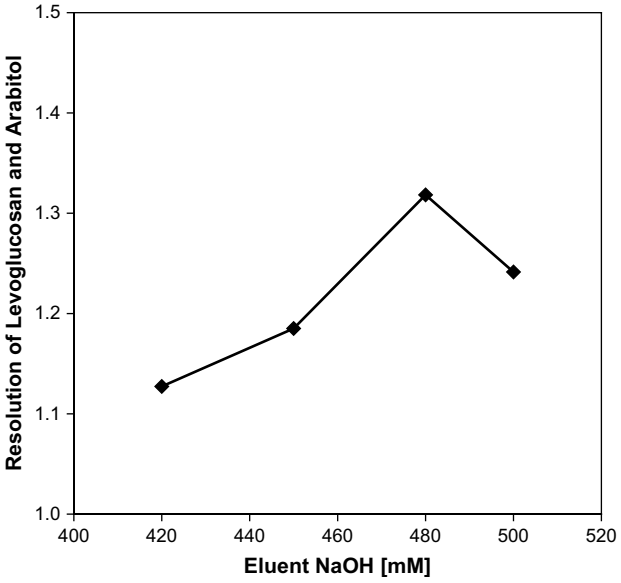

Fig. 1. Resolution of levoglucosan and arabitol peaks as a function of NaOH eluent concentration.

Table 1
Eluent programme. Negative times denote the conditioning of the column.

Time (min)	A% (Water)	B% (1 M NaOH)
−15.0	35	65
−14.9	52	48
0.0	52	48
20.0	52	48
35.0	35	65
45.0	35	65

certain atmospherically relevant saccharidic compounds such as levoglucosan/arabitol (Caseiro et al., 2007) and mannose/glucose (Engling et al., 2006b). Since the PAD cannot separate co-eluting compounds unlike mass spectrometric detection, the chromatographic separation of target analytes is essential for the accurate quantification of the individual compounds. The CarboPac MA1 column is capable to separate several atmospherically relevant monosaccharides including mannose and glucose well (Dionex Application Note 122); hence the optimisation of the current method was focused on the separation of levoglucosan and arabitol.

The effect of the eluent NaOH concentration on the peak resolution of levoglucosan and arabitol was investigated with NaOH concentrations of 270 mM, 420 mM, 450 mM, 480 mM and 500 mM. The peak resolution (R) was calculated following the European Pharmacopoeia recommended method:

$$R = 1.18\left|\frac{t_{\text{Ref. Peak}} - t_{\text{R}}}{W_{50\%,\text{Ref. Peak}} + W_{50\%,\text{R}}}\right|$$

where t_{R} is the retention time of the peak for the resolution, $t_{\text{Ref. Peak}}$ is the retention time of the reference peak for the resolution (a peak after the t_{R}), $W_{50\%,\text{R}}$ and $W_{50\%,\text{ Ref. Peak}}$ are the width of peaks at t_{R} and $t_{\text{Ref. Peak}}$ at 50% of the peak height, respectively. Baseline resolution is defined as R greater than 1.5, though the R value above 1 is acceptable for quantification.

Fig. 1 shows the resolution of levoglucosan and arabitol as a function of NaOH concentration. No R value was obtained for 270 mM as no separation was achieved at this eluent concentration. The R values were greater than 1 for NaOH concentrations above 420 mM, reaching a maximum of 1.3 with the 480 mM solution. On the basis of the determined R values, 480 mM was chosen as the initial eluent NaOH concentration. The eluent programme is summarised in Table 1. The concentration of NaOH was increased from 480 mM at 20 min to 650 mM at 35 min, in order to elute disaccharides and oligosaccharides from the column. Table 2 summarises the R values for the standard compounds used in this study. The R values were greater than 1.3 for all compounds, indicating that the eluent programme is appropriate for the separation of atmospherically relevant saccharidic compounds. Typical chromatograms using the described eluent programme are shown in Fig. 2a (standard), b (autumn ambient aerosol) and c (winter ambient aerosol).

3.2. Limits of detection, reproducibility and quantification parameters of the method

The limit of detection (LOD) was determined as the minimum concentration that was visible on the chromatogram and produced a peak height at least three times the signal to noise ratio. For galactosan and fructose, the minimum visible concentrations were taken as LOD values because they were much higher than $S/N = 3$. The LOD values were in the range of 0.002–0.08 mg L^{-1} corresponding to 0.1–2 ng absolute analyte mass injected using a 25 μL loop (Table 2). These values are somewhat better than the LOD values reported by Caseiro et al. (2007) for their HPAEC–PAD method. The LOD values obtained for this method were converted to equivalent atmospheric concentrations for Hi-Vol sampling at 500 L min^{-1} and 24 h (720 m^3 air). The equivalent atmospheric concentrations are lower than 1 ng m^{-3} except for fructose with 6.5 ng m^{-3}. These LOD values are sufficiently low for the application of the method to atmospheric aerosols, as the concentrations of saccharidic compounds are typically higher than 10 ng m^{-3} in the atmosphere (e.g. Caseiro et al., 2007; Pashynska et al., 2002; Yttri et al., 2007).

The reproducibility of the method was evaluated for the retention time and the peak area of each compound. Relative standard deviations (RSDs) were determined from (1) three consecutive analyses of standard solutions, (2) analyses of standard solutions from nine different analytical days over six months and (3) nine consecutive analyses of a wintertime aerosol sample with high

Table 2
Resolution, limit of detection (LOD), reproducibility and calibration curve correlation coefficient for the developed method.

Compound	Ret. time (min)	Resol.	LOD[a]			Reproducibility								Calibration curves	
			Extract conc. (mg L^{-1})	Injected amount[b] (ng)	Aerosol conc.[c] (ng m^{-3})	Consecutive (0.63 mg L^{-1}, $n = 3$)		Day to day variation (0.63 mg L^{-1}, $n = 9$)		Atmospheric sample (consecutive, $n = 9$, 3 February 2008)					
						Ret. time RSD%	Area RSD%	Ret. time RSD%	Area RSD%	Extract conc. (mg L^{-1})	Aerosol Conc. (ng m^{-3})	Ret. Time RSD%	Area RSD%	Conc. range (mg L^{-1})	R^2
Inositol	8.8	5.0	0.002	0.1	0.2	0.00%	0.4%	0.2%	1.9%	N.D.	N.D.	N.D.	N.D.	0.02–10	0.999
Erythritol	11.3	5.9	0.002	0.1	0.2	0.04%	0.2%	0.3%	2.1%	0.02	1.4	0.3%	15%	0.02–10	0.999
Levoglucosan	14.8	1.3	0.006	0.2	0.5	0.06%	0.5%	0.5%	2.8%	3.4	299	0.1%	1.5%	0.02–10	0.999
Arabitol	15.7	1.9	0.002	0.1	0.2	0.05%	0.2%	0.4%	3.3%	0.04	3.8	0.1%	5.8%	0.02–10	0.999
Mannosan	17.1	3.5	0.004	0.1	0.3	0.06%	0.2%	0.5%	3.5%	0.6	52	0.1%	1.4%	0.02–10	0.999
Mannitol	20.2	1.6	0.005	0.1	0.4	0.04%	1.2%	0.5%	3.2%	0.7	57	0.1%	3.3%	0.02–10	0.999
Mannose	21.7	1.3	0.005	0.1	0.4	0.06%	1.4%	0.7%	4.0%	0.2	17	2.0%	8.5%	0.02–10	0.999
Galactosan	22.9	1.3	0.01	0.3	0.8	0.04%	0.9%	0.7%	3.9%	0.3	28	0.1%	5.0%	0.02–10	0.999
Glucose	24.2	2.1	0.003	0.1	0.2	0.02%	0.7%	0.8%	2.2%	0.1	8.7	0.5%	11%	0.02–10	0.999
Galactose	27.0	1.3	0.003	0.1	0.2	0.08%	0.2%	0.8%	1.4%	0.01	0.6	1.1%	26%	0.02–10	0.999
Fructose	28.6	N.A.	0.08	2	6.5	0.02%	1.0%	0.8%	3.4%	N.D.	N.D.	N.D.	N.D.	0.16–10	0.999

[a] S/N minimum 3.
[b] 25 μm sample loop.
[c] 24 h sample, Hi-Vol sampler (720 m^3 air volume).

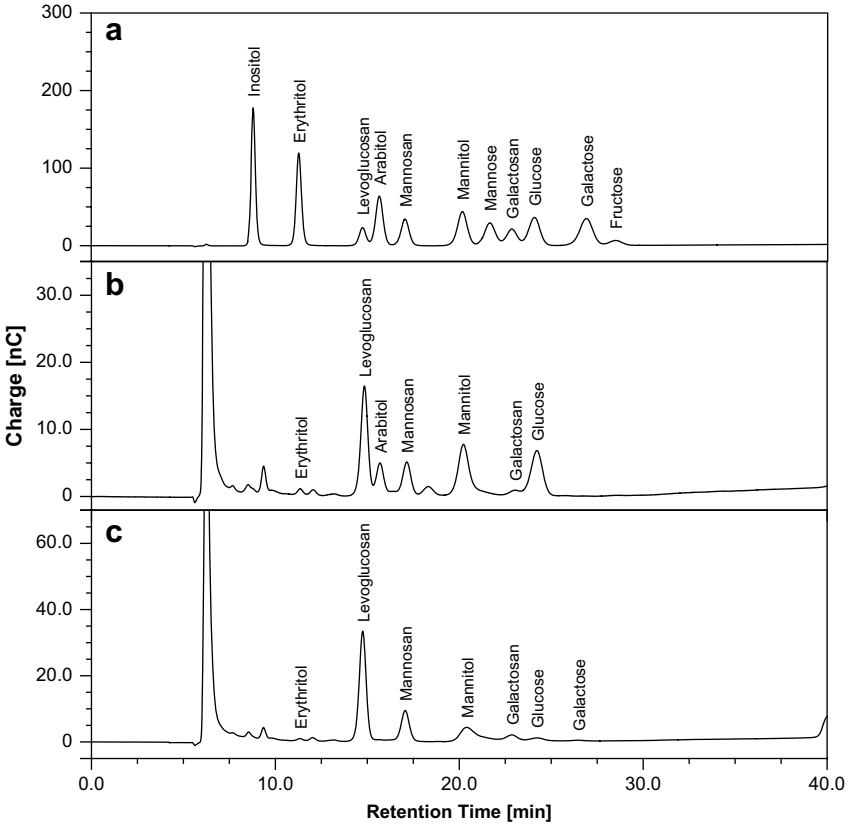

Fig. 2. Chromatograms obtained from the analysis of (a) 5 mg L^{-1} standard solution, (b) autumn PM_{10} sample collected on 6th October 2007 and (c) winter PM_{10} sample collected on 25th December 2007.

levoglucosan content. The obtained RSDs are summarised in Table 2. No RSDs from the wintertime aerosol samples were determined for inositol and fructose, as they were not detected in the samples. The reproducibility of the method was found to be satisfactory for both the standard solutions and the real environmental sample. In total, over 250 samples were collected and analyzed using the developed method during the campaign and very small day to day variation was observed for both the retention times and peak areas, demonstrating the robustness and stability of the method. This indicates that the method can handle a large number of samples without recalibration during a sequence and it requires only an injection of a control standard after several sample injections. It is noted that somewhat higher RSDs found for erythritol and galactose from the atmospheric sample were close to the respective LOD values, yet they were still acceptable considering the concentrations of these compounds in the samples ($\sim$1 ng m^{-3}).

Table 2 summarises the calibration parameters for the method. Calibration curves for tested monosaccharidic compounds showed correlation coefficients (R^2) greater than 0.999 in the range of 0.02–10 mg L^{-1} (10 points) for quadratic regressions, except fructose (0.16–10 mg L^{-1} (8 points), $R^2 > 0.999$). These values are satisfactory for the quantification of the saccharidic compounds investigated in this study.

4. Summary

A simple HPAEC–PAD method for the determination of eleven atmospherically relevant saccharidic compounds was developed and validated in this study. Particular attention was paid to the separation of levoglucosan and arabitol, which were not or insufficiently separated in previous HPAEC–PAD methods. These compounds are now separated near-baseline with a resolution of $R > 1$. The RSDs of peak areas for monosaccharide anhydrides were found to be lower than 1% for standard solutions and lower than 5% for a typical wintertime sample. The peak area RSDs for other saccharidic compounds were also in a similar range except for the compounds which were close to the LOD values.

The method is simple, inexpensive, reliable, sensitive, selective and quantitative for routine analysis of atmospherically important saccharidic compounds. The method can be further coupled to mass spectrometry using a suppressor, providing the possibility for structural elucidation of unknown peaks.

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