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Environmental

Improved HPAE-PAD method for determination of saccharides in atmospheric aerosol samples

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Keywords
Dionex CarboPac PA300-4µm column, biomass burning, WSOC, levoglucosan, galactosan, mannosan

Goal

To develop an improved method to separate 12 saccharides present in atmospheric aerosol samples in 20 min without derivatization by HPAE-PAD

Introduction

Biomass burning is a major source of particulate matter present in atmospheric aerosol. The presence of these particles not only impacts air quality but has hazardous effects on human health. Anhydrosugars, sugar alcohols, monosaccharides, and disaccharides are among the major classes of water-soluble organic compounds (WSOC) in atmospheric aerosols.[1,2] Atmospheric saccharides originate from two main sources: biomass burning (natural or anthropogenic) and natural biogenic detritus.[1,3–6] Saccharides have been proposed as markers to evaluate the contribution of these sources to atmospheric aerosol.[2] The anhydrosugars levoglucosan, mannosan, and galactosan originate from the combustion of cellulose and hemicellulose due to wildfires or residential wood burning.[1,2]

High performance anion exchange chromatography with pulsed amperometric detection (HPAE-PAD) has been used to determine saccharides from atmospheric aerosol samples.[7–12] HPAE-PAD separates native carbohydrates (i.e., underivatized) at high pH (>12) and detects them by PAD on a gold working electrode. HPAE can separate complex mixtures of carbohydrates, and PAD is a powerful detection technique with a large dynamic working range and low detection limits. For complex samples, the high resolving power of HPAE and the specificity of PAD allow the determination of carbohydrates, glycols, sugar alcohols (alditols), and other alcohols such as ethanol and methanol (albeit with much less sensitivity), with little interference from matrix components.

The HPAE-PAD methods for saccharide determination in atmospheric aerosol samples typically use a Thermo Scientific™ Dionex™ CarboPac™ MA1[7] column for separation of anhydrosugars and sugar alcohols. Some studies have used a Dionex CarboPac PA10[9] or a Dionex CarboPac PA1[10] column alone to separate anhydrosugars and monosaccharides. Sometimes, both these columns are used together.[8] However, these methods have drawbacks. In some cases, the resolution between key saccharide pairs, for example arabitol and levoglucosan, is poor.[13] A single column method can result in smaller saccharide coverage.[9] Whereas, using two separate columns in combination makes saccharides analysis cumbersome.[8] We recently developed a single column method,[14] but it has a long run time of 57 min. Therefore, this work was initiated to develop an improved single column method to determine anhydrosugars, simple sugars, and sugar alcohols present in atmospheric aerosol samples. We developed this method using the recently launched Thermo Scientific Dionex CarboPac PA300-4µm column. Results for method linearity, accuracy, and robustness are presented.

Experimental

Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC™ High Pressure Ion Chromatography system using electrochemical detection, including*:
  - Thermo Scientific™ Dionex™ Electrochemical Detector (ED)
  - Thermo Scientific™ Dionex™ Eluent Generator Cartridge (Dionex EGC 500 KOH)
  - Thermo Scientific™ Dionex™ Electrochemical Cell, Reference Electrode with Gasket, and Disposable Working Electrode with Gasket
  - Thermo Scientific™ Dionex™ Detector Compartment Temperature Control
  - Thermo Scientific™ Dionex™ Tablet Control
  - Thermo Scientific™ Dionex™ Vacuum Degas Kit
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 1.5 mL trays, (P/N 079656)
- Sterile assembled micro-centrifuge tubes with screw cap, 1.5 mL (Sarstedt P/N 72.692.005)

* This method can also be executed on a Thermo Scientific™ Dionex™ ICS-6000 system equipped with an electrochemical detector.

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data system (CDS) version 7.2.10

Conditions

Columns	Dionex CarboPac PA300-4µm, 2 × 250 mm column (P/N 303346) Dionex CarboPac PA300-4µm guard column (P/N 303347)
Column temperature	30 °C
Compartment temperature	25 °C
Flow rate	0.275 mL/min
Eluent	15 mM potassium hydroxide
Eluent source	Dionex EGC 500 KOH (P/N 075778)
Working electrode	Gold disposable on PTFE (P/N 066480)
Reference electrode	Ag/AgCl reference electrode (P/N 061879)
Gasket	PTFE, for Disposable Electrode 0.002 in (2 mil) (1 mil = 25.4 µm) (P/N 060141)
Injection volume	2.5 µL (Full_Loop)
Typical backpressure	2,600 psi (100 psi = 698.5 kPa approximately)
Waveform	Carbohydrate 4-Potential Waveform (Table 1)

Table 1. Carbohydrate 4-Potential Waveform for the ED

Time (s)	Potential (V)	Gain	Ramp region	Integration system
0	0.1	Off	On	Off
0.2	0.1	On	On	On
0.4	0.1	Off	On	Off
0.41	-2	Off	On	Off
0.42	-2	Off	On	Off
0.43	0.6	Off	On	Off
0.44	-0.1	Off	On	Off
0.5	-0.1	Off	On	Off

Reference electrode used in Ag mode (Ag/AgCl reference).

Reagents

- Levoglucosan (Toronto Research Chemicals, P/N A168400)
- Mannosan (Toronto Research Chemicals, P/N A652500)
- Galactosan (Toronto Research Chemicals, P/N A641000)
- Arabitol (Sigma, P/N A3381)
- Erythritol (Pfanstiehl, P/N E100)
- Xylitol (Sigma, P/N X3375)
- Sorbitol (Sigma, P/N S1876)
- Galactitol (Pfanstiehl, P/N RGG100)
- Mannitol (Sigma, PN M9546)
- Galactose (Sigma, P/N G0625)
- Glucose (Fisher, P/N 1910-01)
- Mannose (Sigma, P/N M6020)
- Fructose (Sigma P/N F2543)
- Sucrose (Sigma P/N 84097)
- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistivity or better

Preparation of solutions and reagents

- Atmospheric aerosol matrix sample: Normally, atmospheric aerosol samples are prepared using high-volume air samplers, but here, an atmospheric aerosol matrix sample was prepared by using passive diffusion on a 3.7 cm Whatman™ GF/A filter paper (Sigma P/N WHA1820037). The filter paper was attached to a vehicle that moved for ~2 h in San Francisco Bay Area traffic. The diffused saccharides were extracted in 10 mL DI water using sonication for 10 min. An untreated control was prepared in the same manner using untreated filter paper.
- Simulated atmospheric aerosol sample: A simulated atmospheric aerosol sample was prepared by spiking saccharides into the atmospheric aerosol matrix sample (Table 2). Spiked amounts were based on a reported composition.[7]

Table 2. Composition of the simulated atmospheric aerosol sample

Saccharide	Amount (mg/L)
Erythritol	0.02
Levoglucosan	3.4
Arabitol	0.04
Mannosan	0.6
Mannitol	0.7
Galactosan	0.3
Mannose	0.4
Glucose	0.1
Galactose	0.01

- Calibration standard solutions: Stock solutions containing 1,000 mg/L of each analyte of interest in DI water were prepared in 125 mL polypropylene bottles. The standard stock solutions or secondary standards containing 5 mg/L or 0.05 mg/L were used directly for making calibration standards for this study. The calibration standards used here were 0.025, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 mg/L.

Robustness study

Method robustness was evaluated by examining retention time, peak asymmetry, and resolution after imposing small variations (±10%) in procedural parameters (e.g., flow rate, eluent concentration, column temperature). A standard mixture containing 15 mg/L of each analyte was injected in triplicate for each condition. The same procedure was applied to another column set from a different lot.

The variations tested were as follows:

- Flow rate at 0.25 mL/min, 0.275 mL/min, and 0.3 mL/min
- Eluent concentration at 13.5 mM, 15 mM, and 16.5 mM
- Column temperature at 27 °C, 30 °C, and 33 °C [Note—Because the Dionex Integrion system does not have column cooling capacity, for testing lower temperature conditions the columns were simply allowed to equilibrate with the room temperature which was 27 °C and 26.1 °C for columns 1 and 2, respectively].

Results and discussion

Saccharides present in atmospheric aerosols were separated on a Dionex CarboPac PA300-4µm column. Figure 1 shows good separation of 12 saccharides, which is completed in less than 20 min. The speed of this separation is a significant improvement over other methods used for this purpose. The type of analytes separated include sugar alcohols, anhydrosugars, and neutral sugars. In addition to the improved speed, electrolytically produced eluent makes the method convenient and automated. Moreover, the lower eluent concentration used in this method, as compared to the methods using the Dionex CarboPac MA1 column, reduces waste and improves process economics. Fructose and sucrose peaks elute close to a dip in the baseline, which distorts their peak shape. This dip is due to the difference in dissolved oxygen in the eluent compared to the sample and is commonly referred to as the “oxygen dip.” If better peak shape is needed, the eluent concentration and/or temperature can be changed to move the fructose and sucrose peaks away from the oxygen dip. The impact of eluent concentration and temperature will be discussed in the section on method robustness.

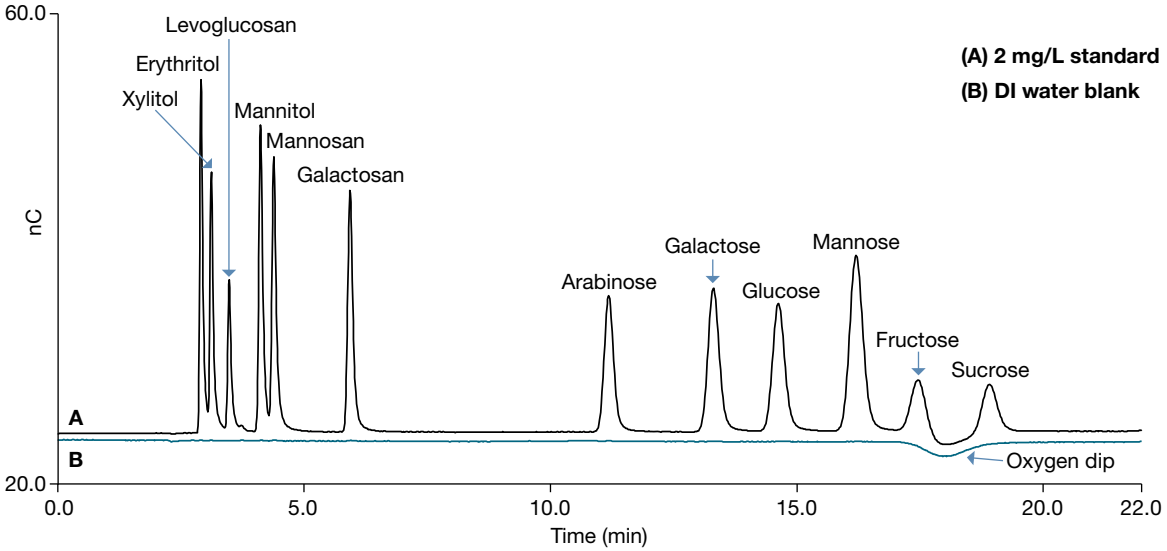

Figure 1. Separation of a 12-saccharide standard using a Dionex CarboPac PA300-4µm column

Table 3 contains retention time and resolution data for all 12 saccharides. The minimum peak resolution is 1.77 (between mannitol and mannosan). The resolutions obtained using the method described here are suitable for quantitation of these 12 saccharides.

A simulated matrix sample, prepared as described in the methods section, was spiked using a known composition of a simulated atmospheric aerosol sample. The spiked amounts are based on a literature report describing the composition of the atmospheric aerosol.[7] Figure 2 shows a separation of this simulated atmospheric aerosol sample.

Table 3. Retention time and resolution data for 12 saccharides

Peak no.	Peak name	RT (min)	Resolution
1	Erythritol	2.91	1.86
2	Xylitol	3.12	2.99
3	Levoglucosan	3.48	4.75
4	Mannitol	4.13	1.77
5	Mannosan	4.40	8.96
6	Galactosan	5.97	19.1
7	Arabinose	11.2	5.45
8	Galactose	13.4	2.96
9	Glucose	14.7	3.22
10	Mannose	16.3	2.43
11	Fructose	17.7	2.38
12	Sucrose	19.0	

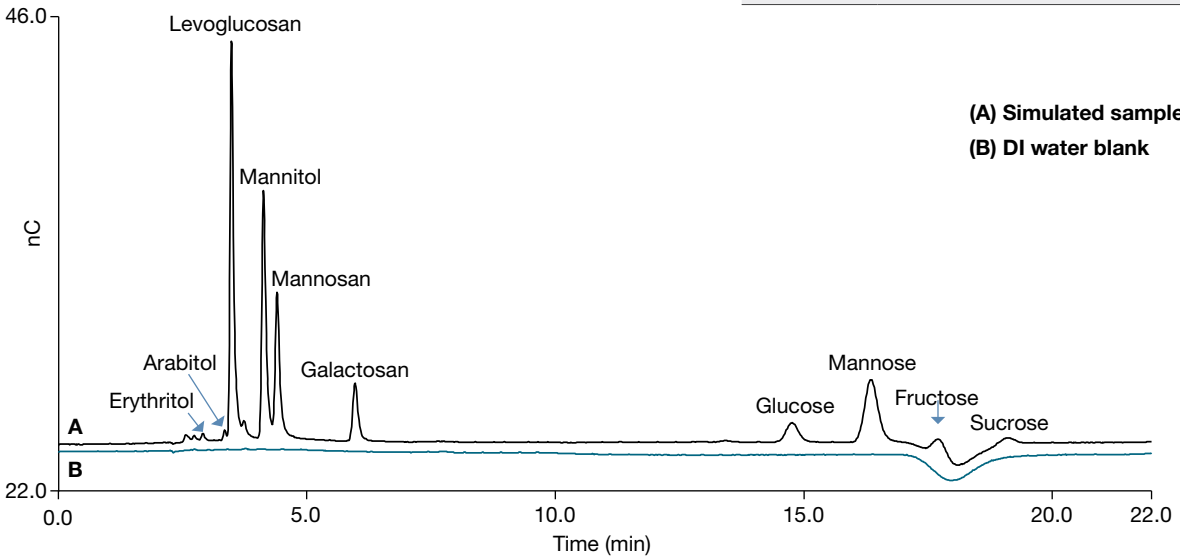

Figure 2. Simulated atmospheric aerosol sample

Precision and linearity

Method precision for retention time, as well as peak area, was measured for the 12 saccharides. Data contained in Table 4 show good retention time as well as peak area precision with all RSD values ranging from 0 to 3.6%.

Method linearity was tested at concentration levels ranging from 0.05 to 20 mg/L. The concentration ranges, the number of levels, and the coefficient of determination values are included in Table 5. The results show good linearity with coefficient of determination values ranging from 0.991 to 0.999. As examples, linear curve fits for the levoglucosan and fructose calibration data are shown in Figure 3A and Figure 3B, respectively.

Table 4. Retention time and peak area RSDs for 12 analytes using 0.5 mg/L standard (n=3)

Sample (mg/L)		RSD											
		Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
5	RT	0.16	0.15	0.13	0.11	0.11	0.00	0.04	0.03	0.05	0.03	0.04	0.00
	Peak area	3.6	2.5	1.3	3.2	2.0	2.4	1.8	1.9	1.9	2.5	1.5	2.1

Abbreviations used: Ery—Erythritol; Xyl—Xylitol; Levo—Levoglucosan; Mannit—Mannitol; Manno—Mannosan; Galacto—Galactosan; Ara—Arabinose; Gal—Galactose; Glc—Glucose; Man—Mannose; Fru—Fructose; Suc—Sucrose

Table 5. Method calibration data (n=3)

Peak no.	Peak name	Conc. range (mg/L)	No. of levels	Coeff. of determination (r^2)
1	Erythritol	0.05–5	7	0.999
2	Xylitol	0.05–5	7	0.998
3	Levoglucosan	0.2–10	6	0.998
4	Mannitol	0.05–5	7	0.999
5	Mannosan	0.05–10	8	0.999
6	Galactosan	0.2–10	6	0.999
7	Arabinose	0.2–10	6	0.997
8	Galactose	0.2–10	6	0.999
9	Glucose	0.2–25	8	0.999
10	Mannose	0.2–5	5	0.999
11	Fructose	0.5–20	5	0.991
12	Sucrose	0.5–20	5	0.999

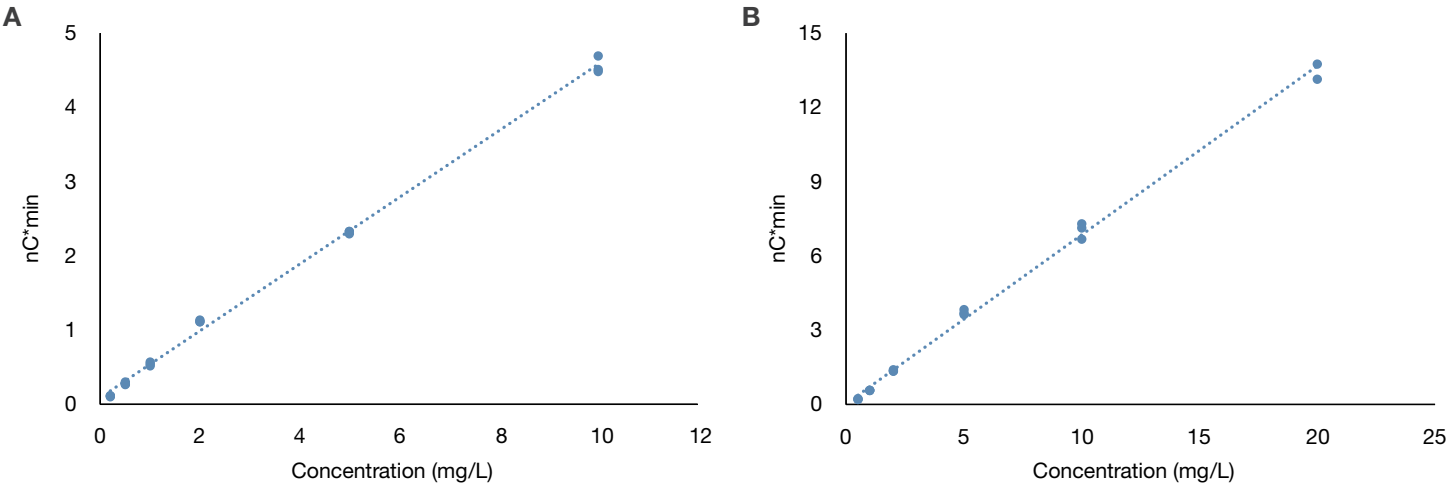

Figure 3. (A) calibration plot for levoglucosan (n=3); (B) calibration plot for fructose (n=3)

Accuracy

To determine method accuracy, atmospheric aerosol matrix samples were spiked with two different concentration levels of the 12 saccharides. Calculated recoveries are summarized in Table 6. Both spike levels showed good recoveries ranging from 80 to 110%, indicating good method accuracy.

Table 6. Spike recovery studies (n=3)

Spike (mg/L)	Recovery (%)											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
0.5	108	102	84	108	106	90.1	80.4	87.1	82.9	90.0	106	95.8
5	102	103	111	100	103	99.9	101	98.1	97.9	93.4	110	97

Abbrevations used: Ery—Erythritol; Xyl—Xylitol; Levo—Levoglucosan; Mannit—Mannitol; Manno—Mannosan; Galacto—Galactosan; Ara—Arabinose; Gal—Galactose; Glc—Glucose; Man—Mannose; Fru—Fructose; Suc—Sucrose

Robustness

Assay robustness was studied by varying method parameters by ±10% and measuring differences in three chromatographic parameters: retention time, peak asymmetry, and resolution. Assay robustness was studied using two columns. Data contained in Tables 7 and 8 generally show minimal impact of changes in method parameters. This indicates that the method is robust to potential variations encountered in method conditions. Of the 12 saccharides studied here, only the chromatography of fructose and sucrose was significantly impacted as resolution varied with column temperature and eluent concentration. Reduction in temperature to 27 °C led to a significant loss of resolution between sucrose and fructose (Figure 4, red trace). Whereas increasing the temperature to 33 °C moved the fructose peak away from the sucrose peak and closer to the mannose peak (Figure 4, blue trace). Resolution between fructose and sucrose dropped significantly when eluent concentration was increased to 16.5 mM (Figure 5, red trace). Reducing the eluent concentration moved the fructose peak closer to the mannose peak (Figure 5, blue trace), which is similar to the effect of increasing temperature. This information is advantageous as both peaks elute close to the oxygen dip. Modulation of elution behavior may be necessary for some columns as the dip represents the oxygen permeability volume of the column, which will vary from column to column. For example, if the oxygen dip occurs below one of the two peaks, then separation between sucrose and fructose peaks can be increased by reducing the eluent concentration or increasing the temperature.

Table 7. Method robustness studied on column 1 using a standard containing 0.5 mg/L of each saccharide (n=3)

	Retention time % difference											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10% higher eluent	0.0	0.1	-0.1	-0.1	-0.2	-0.4	-2.3	-2.3	-2.8	-3.6	-1.3	-3.5
10% lower eluent	0.0	0.3	0.3	0.3	0.4	0.8	3.3	3.3	3.8	5.0	1.8	5.0
10% higher flow	-8.3	-8.3	-8.4	-8.5	-8.4	-8.4	-8.2	-8.3	-8.2	-8.0	-8.7	-8.1
10% lower flow	10.0	10.1	10.2	10.4	10.4	10.6	10.8	10.9	10.9	11.0	11.0	11.1
10% higher temperature	-0.4	-0.5	-1.3	-1.3	-2.5	-3.8	-2.4	-2.9	-3.6	-3.5	-7.4	-2.7
10% lower temperature	0.6	0.9	1.4	1.5	2.5	3.9	3.2	3.8	4.3	4.4	7.8	3.7
	Peak asymmetry % difference											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10% higher eluent	1.1	-5.1	0.4	-0.3	2.1	0.7	0.6	-0.3	1.8	0.6	-4.6	3.1
10% lower eluent	6.6	-7.1	-2.0	0.3	4.1	0.2	-0.3	-0.9	0.6	-3.4	1.4	-4.0
10% higher flow	-0.7	-4.3	0.0	1.8	1.1	-2.6	-1.4	-0.9	1.2	-2.3	-1.8	0.3
10% lower flow	7.3	2.8	2.4	3.0	0.9	-1.0	0.6	-0.6	1.5	0.3	-0.6	-0.6
10% higher temperature	-0.5	-3.4	1.5	-11.0	0.2	1.0	0.0	-0.6	1.2	-10.5	7.3	1.1
10% lower temperature	1.4	-6.5	-3.1	8.8	5.5	-1.4	-0.8	-0.3	0.3	-0.6	-14.7	0.3

Abbrevations used: Ery—Erythritol; Xyl—Xylitol; Levo—Levoglucosan; Mannit—Mannitol; Manno—Mannosan; Galacto—Galactosan; Ara—Arabinose; Gal—Galactose; Glc—Glucose; Man—Mannose; Fru—Fructose; Suc—Sucrose

Table 7 (continued). Method robustness studied on column 1 using a standard containing 0.5 mg/L of each saccharide (n=3)

	Resolution % difference										
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10% higher eluent	1.4	-1.4	-0.1	-0.9	-1.1	-2.6	0.4	-4.6	-7.5	28.9	-30.9
10% lower eluent	3.6	-0.1	0.3	0.7	0.3	3.8	0.7	6.1	11.8	-36.2	46.1
10% higher flow	-2.4	-3.3	-3.1	-1.6	-2.9	-1.3	-1.6	-0.3	1.0	-9.1	7.3
10% lower flow	3.6	2.5	3.1	3.1	2.4	2.6	3.2	2.3	3.9	4.4	5.2
10% higher temperature	-2.8	-7.0	1.7	-18.4	-3.3	3.6	-0.8	-4.1	4.0	-49.0	73.2
10% lower temperature	4.1	5.0	-0.2	15.3	3.5	-1.5	2.8	5.0	0.5	45.2	-48.2

Abbrevations used: Ery—Erythritol; Xyl—Xylitol; Levo—Levoglucoosan; Mannit—Mannitol; Manno—Mannosan; Galacto—Galactosan; Ara—Arabinose; Gal—Galactose; Glc—Glucose; Man—Mannose; Fru—Fructose

Table 8. Method robustness studied on column 2 using a standard containing 0.5 mg/L of each saccharide (n=3)

	Retention time % difference											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10% higher eluent	-0.1	-0.2	-0.2	-0.3	-0.4	-0.6	-2.7	-2.7	-3.2	-4.1	-1.4	-4.1
10% lower eluent	0.1	0.1	0.2	0.2	0.4	0.7	3.0	3.1	3.6	4.7	1.7	4.7
10% higher flow	-8.2	-8.3	-8.2	-8.5	-8.4	-8.6	-8.6	-8.6	-8.6	-8.5	-8.8	-8.6
10% lower flow	10.0	10.0	10.2	10.3	10.3	10.4	10.4	10.5	10.4	10.4	10.8	10.5
10% higher temperature	-0.4	-0.6	-1.2	-1.2	-2.4	-3.6	-2.5	-3.0	-3.6	-3.7	-7.0	-2.9
10% lower temperature	0.7	1.0	1.9	2.1	3.9	5.6	3.7	4.7	5.5	5.4	ND	4.1
	Peak asymmetry % difference											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	Suc
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10% higher eluent	1.3	4.4	4.6	1.1	1.2	3.3	2.5	-0.8	5.0	5.7	-14.2	1.7
10% lower eluent	1.9	3.4	0.0	3.7	1.0	1.2	0.0	2.2	4.7	-5.2	0.6	-2.0
10% higher flow	2.4	1.6	-2.6	1.7	0.7	0.9	1.4	-0.8	1.5	0.0	-0.6	-0.9
10% lower flow	3.2	6.0	1.4	2.3	-0.2	2.1	0.0	-0.3	0.3	0.9	-1.2	0.0
10% higher temperature	1.1	4.1	4.6	-8.2	-0.5	2.8	1.4	-1.4	3.8	-7.2	2.9	-1.1
10% lower temperature	2.9	5.3	7.7	11.1	1.0	1.2	1.4	1.9	4.4	1.7	ND	-1.1
	Resolution % difference											
	Ery	Xyl	Levo	Mannit	Manno	Galacto	Ara	Gal	Glc	Man	Fru	
Method condition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
10% higher eluent	-2.4	-1.2	-0.6	-2.0	-1.1	-3.4	-0.1	-5.8	-10.2	37.7	-34.2	
10% lower eluent	-1.1	0.7	-0.5	1.8	0.3	3.4	0.1	5.5	10.4	-31.9	43.4	
10% higher flow	-2.4	-1.5	-3.3	-1.5	-2.7	-2.1	-2.0	-1.7	-1.8	-5.3	1.6	
10% lower flow	-1.5	0.4	0.3	0.4	0.7	1.3	2.2	1.3	1.5	5.9	-1.5	
10% higher temperature	-4.5	-6.9	1.4	-15.6	-3.4	2.1	-1.6	-5.5	1.3	-37.8	68.5	
10% lower temperature	-0.6	5.1	-3.2	20.7	2.4	-4.4	2.6	5.7	-2.7	60.4	ND	

Abbrevations used: Ery—Erythritol; Xyl—Xylitol; Levo—Levoglucoosan; Mannit—Mannitol; Manno—Mannosan; Galacto—Galactosan; Ara—Arabinose; Gal—Galactose; Glc—Glucose; Man—Mannose; Fru—Fructose; Suc—Sucrose

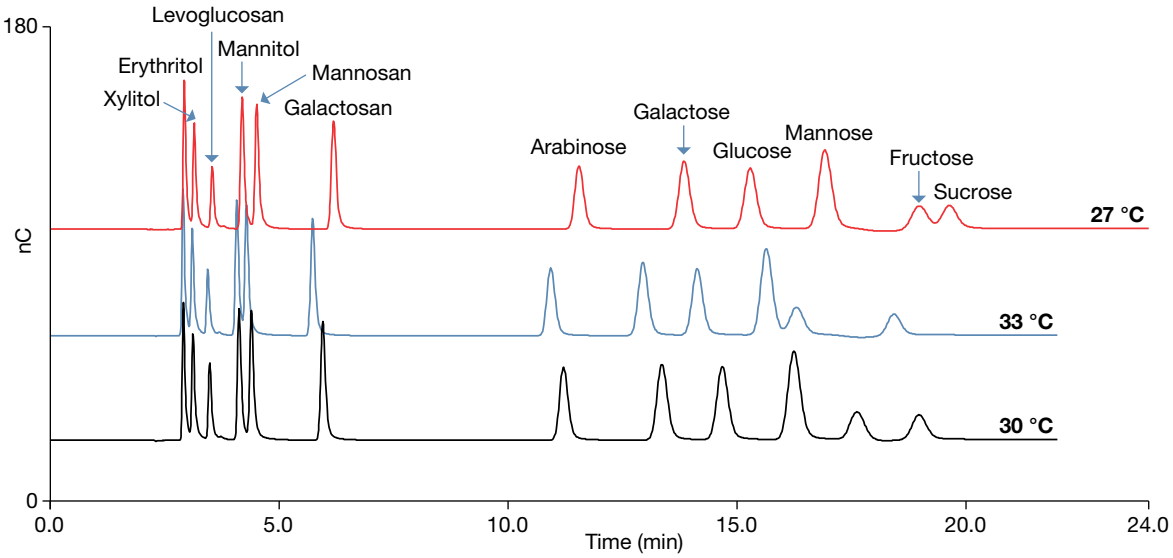

Figure 4. Effect of temperature on saccharide separation

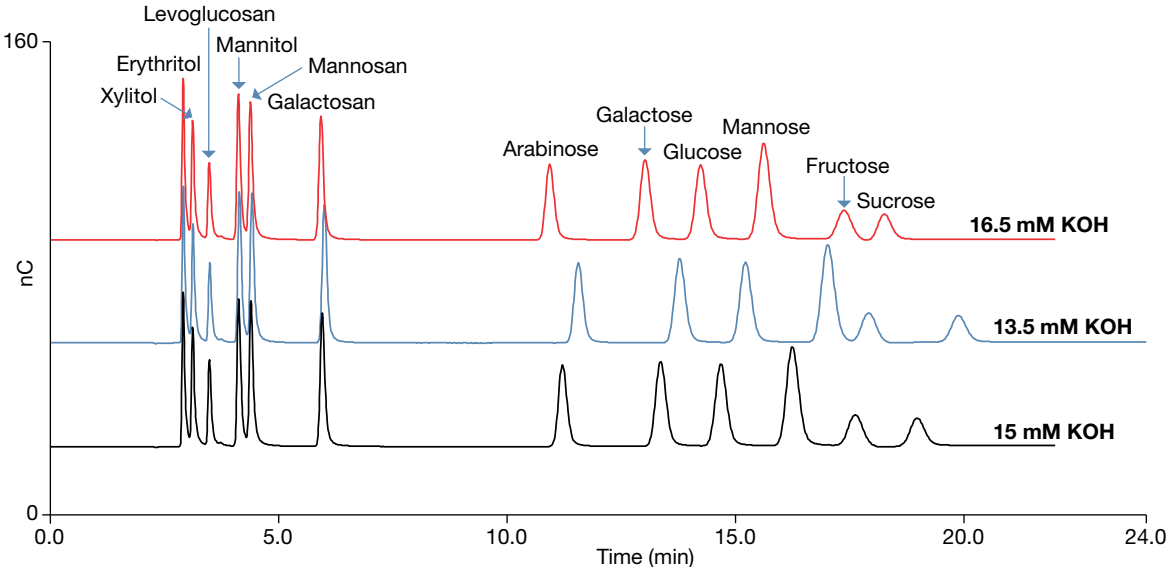

Figure 5. Effect of eluent concentration on saccharide separation

Conclusion

We have described an improved method that separates 12 saccharides present in atmospheric aerosol samples in 20 min. The resolved saccharides include anhydrosugars, sugar alcohols, and mono- and disaccharides. The run time of this method is significantly shorter than other reported methods and can be paired with electrolytic eluent generation to simplify the analysis. The determination of these analytes is greatly simplified as this is a single-column method. The method shows good precision, linearity, and accuracy. This method can be used for routine automated analysis of atmospheric aerosol samples.

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