A New Solution for Fast and Rugged Biofuel Carbohydrate Analysis

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INTRODUCTION

The rapidly growing biofuel industry has a need for a fast, robust approach for the analysis of carbohydrate contents in biomass samples. The CarboPac® SA10 column is a new porous, strong anion-exchange column developed to provide superior separations for biofuel sugars. The innovative column design allows fast, high-resolution separations of mono- and disaccharides. Eight common biofuel sugars are separated on this column within 7 min; significantly faster than any other existing methods. By using a 0.4 µL injection valve and a thicker ED gasket, quantitative analysis of high-concentration corn stover hydralysate sample can be achieved on this column after just 100 fold sample dilution. The column can also be used for efficient carbohydrate separations in other fields, including food and beverage, and biotech/pharmacutical industries.

COLUMN CHEMISTRY

The new CarboPac SA10 column is composed of a wide-pore macroporous substrate coated with a strong anion-exchange layer of latex nano beads. (Figure 1) The substrate resin is ethylvinylbenzene crosslinked with divinylbenzene with macropores throughout the bead. The highly porous structure results in increased surface area, providing higher loading capacity. The nanobead anion-exchange layer which coats the entire surface is functionalized with an alkanol quaternary ammonium group. This layer has a controlled thickness which results in excellent mass-transfer characteristics and consequently, high-efficiency peaks. The combination of the high capacity provided by the substrate and the new internal chemistry of the nanobead functionality delivers high-resolution and short analysis time for the common sugars of interest in biofuel applications.

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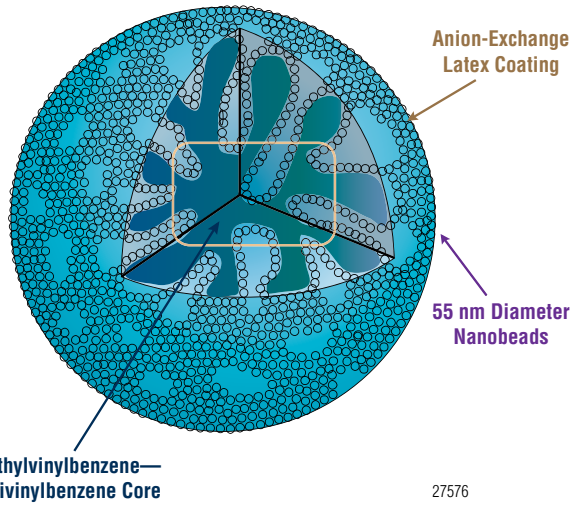

Figure 1. CarboPac SA10 resin structure.

COLUMN SPECIFICATIONS

Column Dimension:	4 × 250 mm
Substrate Resin Size:	6 µm
Pore Size:	2000 Å
Latex Size:	55 nm
Latex Functional Group:	Quaternary ammonium
Typical Eluents:	Potassium hydroxide or sodium hydroxide
Stable pH range:	0–14
Temperature Range:	4–60 °C
Maximum Pressure:	3500 psi
Organic Solvent Limit:	Compatible with 100% common organic solvents

SYSTEM REQUIREMENT

The CarboPac SA10 column can be used on any HPAE-PAD system. For this study, a Dionex ICS-3000 system was used, which includes a SP or DP pump, AS autosampler, EG eluent generator with a KOH or NaOH cartridge, and DC thermal compartment with an ED detector cell. Ag/AgCl was used as reference electrode and Au as working electrode. The quadruple waveform was used for detection of carbohydrates. For high concentration samples, a thicker ED gasket (62 mil) was used to lower the detection sensitivity and increase the high end of linearity. An internal injection valve with 0.4 µL injection volume was used to minimize the sample amount loaded to the column (P/N 072050).

FAST AND HIGH-RESOLUTION SEPARATION OF BIOFUEL SUGARS

Eight common biofuel sugars can be separated within 7 min, significantly faster than any other existing method (Figure 2).

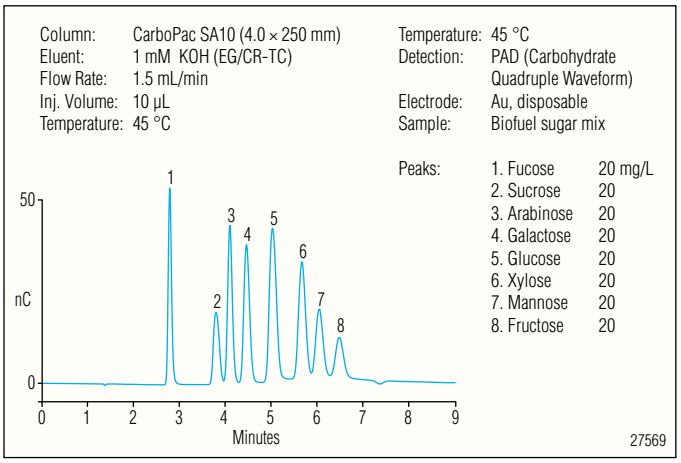

Figure 2. Separation of biofuel sugars on the CarboPac SA10 column.

Temperature has significant effects on resolution of the sugars. Optimal resolution was achieved at 45 °C (Figure 3).

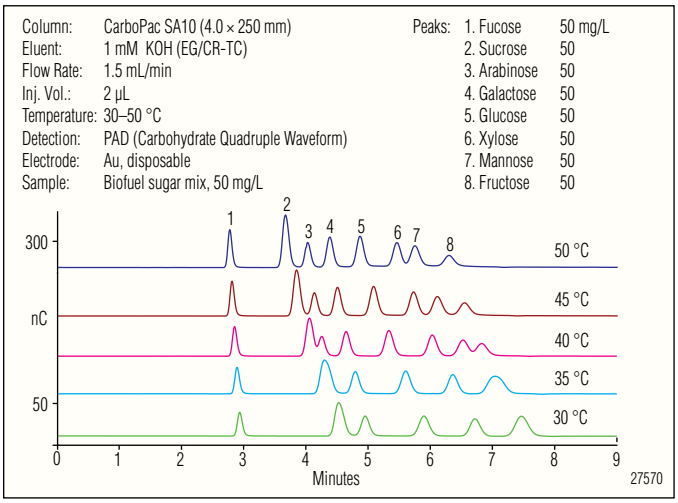

Figure 3. Separation of biofuel sugars under different temperatures.

COLUMN RUGGEDNESS

The high-quality resin/latex packing ensures remarkable stability of the CarboPac SA10 column, providing thousands of injections with high reproducibility. Figure 4 shows the performance of the column over one thousand injections. With high-purity KOH eluent generated by EG, washing with high-concentration KOH and reconditioning the column after each injection is not required. Trace amounts of carbonate can accumulate on the column over time, causing the retention time to shift. Therefore, it is recommended to wash the column with 100 mM KOH after every 30–40 injections to remove this contaminant.

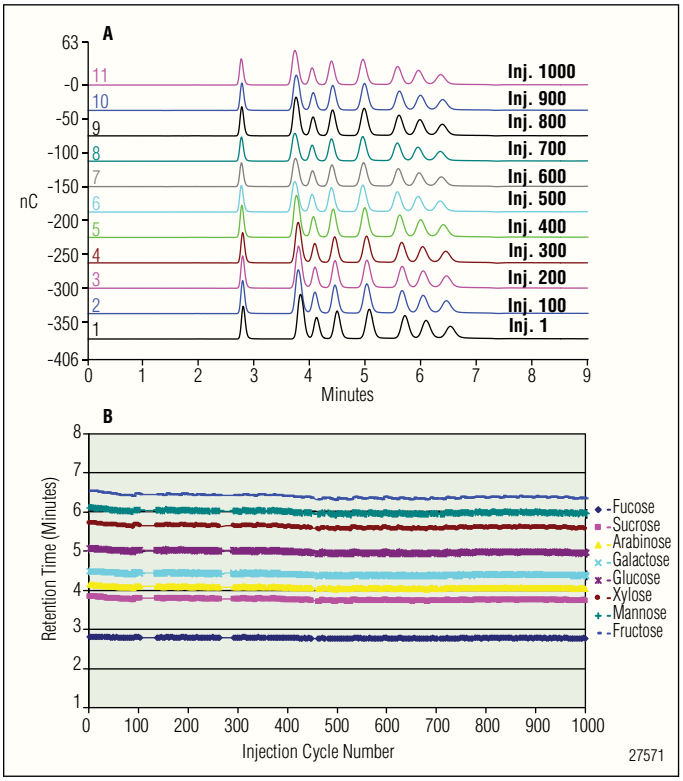

Figure 4. Ruggedness of column, R.T. vs. Inj.# over 1000 injections.

LINEARITY

With a 0.4 µL internal injection valve and a 62 mil ED gasket, linear response can be achieved from 5 ppm to 1000 ppm for the major biofuel sugars (see Figure 5).

ANALYSIS OF CORN STOVER HYDROLYSATE SAMPLES

Pulsed amperometric detection (PAD) is well known for high sensitivity. Biomass samples often contain high concentration (over 100 g/L) sugar contents, which usually require a dilution factor of 1000 to avoid saturating the column or the detector. By reducing the injection volume to 0.4 µL with an internal injection valve, and reducing the detector sensitivity with 62 mil thick ED gasket, corn stover hydrolysate sample with ~150 g/L total sugar concentration can be analyzed quantitatively on the column after 100× dilution (Figure 5).

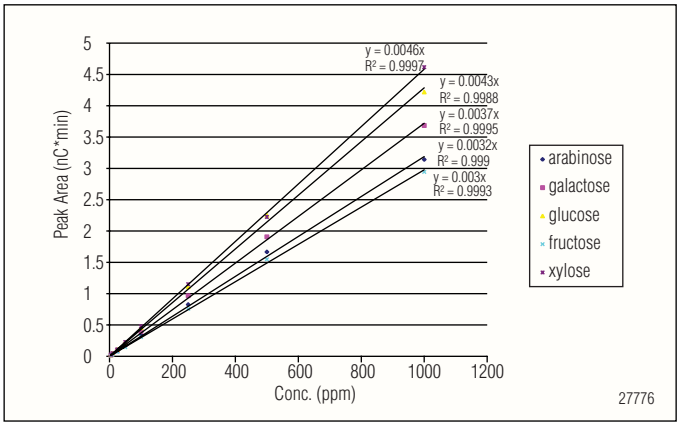

Figure 5. Linearity on the CarboPac SA10.

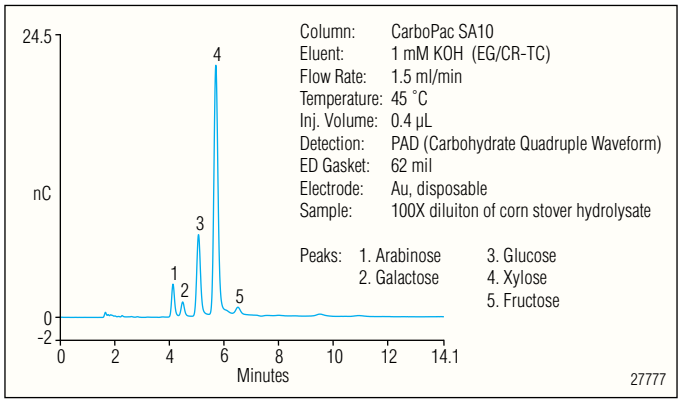

Figure 6. Analysis of corn stover hydrolysate on the CarboPac SA10.

OTHER APPLICATIONS

The CarboPac SA10 column can be used in many other applications for separation of mono-, disaccharides, and their derivatives. The column can be used to separate sugars found in food and drink products (Figure 7).

Table 1. Quantitave Analysis of Sugar Contents in Corn Stover Hydrolysate

	Peak Area (nC*min)			Average Peak Area (nC*min)	Diluted Sample Conc.	Original Sample Conc.	RSD
	Inj.1	Inj.2	Inj.3		ppm	g/L	
Arabinose	0.355	0.353	0.367	0.358	111.98	11.2	2.11%
Galactose	0.18	0.183	0.188	0.184	49.64	4.96	2.20%
Glucose	1.126	1.111	1.155	1.131	262.95	26.3	1.98%
Xylose	3.76	3.715	3.879	3.785	822.75	82.3	2.24%
Fructose	0.102	0.104	0.109	0.105	35.00	3.50	3.43%

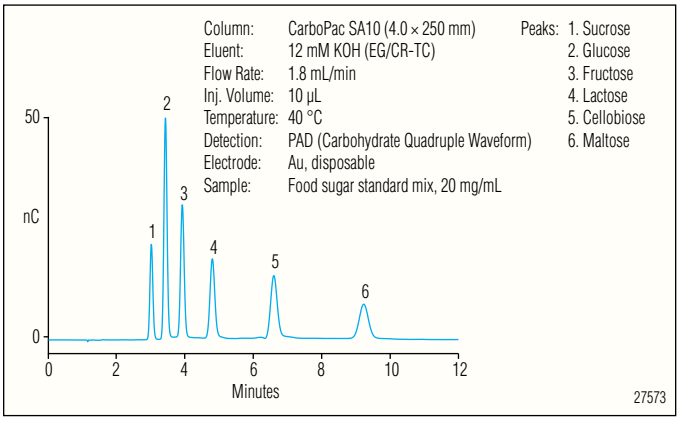

Figure 7. Separation of food sugars on the CarboPac SA10 column.

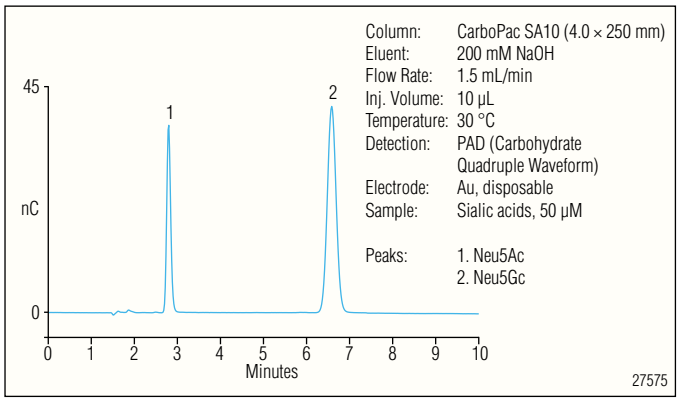

Figure 8. Separation of sialic acids on the CarboPac SA10 column.

CONCLUSIONS

- The CarboPac SA10 column can provide fast, high-resolution separation for biofuel carbohydrates. Eight common mono- and disaccharides in biofuel studies can be separated within 7 min on this column.
- Dilution requirements are minimized for biomass samples containing high-conc. carbohydrate content. When using a 0.4 µL injection valve and a 62 mil ED gasket, a corn stover hydrolysate sample with ~150 g/L total sugar concentration can be quantitatively analyzed on this column after 100× dilution.
- The CarboPac SA10 column can also be used for fast, high-resolution separation of mono- and disaccharides in foods and beverages, and in pharmaceutical samples.

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