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RAPID HIGH-RESOLUTION SEPARATION OF OLIGOSACCHARIDES ON SILVER FORM CATION-EXCHANGE RESINS*

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SUMMARY

The effect of silver as a counter-ion for the aqueous separation of oligosaccharides on cation-exchange resins has been investigated. Silver form cation-exchange resins retain oligosaccharides to a greater extent than the calcium form of the same resins, resulting in a greater number of oligosaccharides being separated. By varying the amount of silver placed on the resin the amount of separation and column efficiency can be optimized. By using the optimum silver loading technique, the operating range, *i.e.*, the number of oligosaccharides separated, has been increased by a factor of two for 4, 5, 6 and 8% cross-linked resins.

INTRODUCTION

Corn-derived oligosaccharides have been separated on calcium form 4% cross-linked cation-exchange resins using water as the sole eluent[1–3]. When operated at low flow-rates the calcium form column separates the oligosaccharides in corn syrups up to a degree of polymerization (DP) of 8. The remaining higher-molecular-weight saccharides elute in the void volume of the column as a single peak at the beginning of the chromatogram. While the resolution of the separation is generally excellent for dextrose and maltose, the resolution of the higher corn-derived oligosaccharides deteriorates markedly after maltotriose and again even more markedly after maltohexaose. These sudden changes in resolution are probably due to the unique helical structure of α-1-4 linked corn-derived oligosaccharides since no corresponding effect has been observed for the separation of cellulose-derived oligosaccharides[4] or for those derived from inulin.

In addition to the resolution losses caused by the structure of corn-derived oligosaccharides, considerable losses in efficiency are also encountered with increases in flow-rate on calcium form columns. Efficiency losses on the order of 50% are not uncommon for a two-fold increase in flow-rate.

Due to these losses and to the rather high compressibility of 4% cross-linked

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resins, usable high-speed separation of corn-derived oligosaccharides is usually limited to DP 1 through DP 5 with analysis times of 15–20 min.

Since some of our earlier work[2] indicated that the number of oligosaccharides separated by a given resin could be doubled with the use of silver as the counter-ion, it was decided to study this system further to see if more mechanically stable and efficient resins could be used to improve the quality of the separation and further reduce the time of the analysis.

EXPERIMENTAL

Materials

The chromatographic resins Aminex A-7 (7–11 μm), Aminex A-5 (10–15 μm), Aminex 50W-X4 (10–15 μm), and an experimental 6% cross-linked, 10–15-μm resin were obtained from Bio-Rad Labs. (Richmond, CA, U.S.A.). The HC-40 (10–15 μm) resin was obtained from Hamilton (Reno, NV, U.S.A.). The silver nitrate used for resin preparation was reagent grade from Mallinckrodt (St. Louis, MO, U.S.A.).

Chromatographic grade tubing (60 cm × 7.8 mm I.D.) was obtained from Waters Assoc. (Milford, MA, U.S.A.) and 30-cm columns were cut from this stock size. Chromatographic end fittings (Cat. No. 6-1Z2HBZ7-3) were obtained from Parker-Hannifin (Huntsville, AL 35802, U.S.A.).

Instrumentation

The automated liquid chromatographic system used in this study consisted of a Waters Model ALC201 equipped with a Model 401 differential refractometer and a 1000-lbs. solvent delivery system (Waters Assoc.), a System I computing integrator (Spectra-Physics, Santa Clara, CA, U.S.A.), an Omniscribe Model 5211-12 dual-pen recorder (Houston Instruments, Austin, TX, U.S.A.) and a custom-built autosampler/system controller of our own design. Details of this system have been described in a previous paper[2].

Resin preparation

Before conversion to the silver form the resin of choice is degassed using a 1:4 slurry of resin in deionized water under aspirator vacuum for 30 min. Following degassing, the resin is transferred to a 350-ml medium porosity sintered glass büchner funnel and the excess water is drawn through the resin bed. The resin is then washed with successive 200-ml portions of 0.5, 1.0, and 2.0 M HNO_3. Each wash is allowed to stand on the resin for 20 min before being drawn through the resin bed. Finally the resin is washed with three 200-ml washes of deionized water as in the previous step.

Since silver form resins perform more efficiently at less than 100% loading, conversions are carried out using equilibrium techniques. In order to convert resins to the desired silver level the following equations and equilibrium constants are used.

The standard equation for silver–hydrogen ion-exchange equilibria is

$$K = \frac{M_{H^+}}{M_{Ag^+}} \times \frac{\%\ \text{Ag resin}}{\%\ \text{H resin}} \quad (1)$$

where K is the equilibrium constant, M_{H^+} is the final molar concentration of H^+,

M_{Ag^+} is the final molar concentration of Ag^+, % Ag resin is the percentage of the resin in the silver form and % H resin is the percentage of the resin in the hydrogen form. For 8% cross-linked resins, the value of 5.84 has been reported[5] for K. For 6, 5 and 4% cross-linked resins the values of K were experimentally determined to be 5.3, 5.0 and 3.0, respectively. By rearranging eqn. 1 and inserting the desired values of silver and hydrogen loading, the final Ag^+ concentration can be calculated using eqn. 2.

$$M_{Ag^+}\text{ (final)} = \frac{M_{H^+}}{K} \times \frac{\%\text{ Ag resin}}{\%\text{ H resin}} \tag{2}$$

Using eqn. 2 along with the amount and the capacity of the resin, the initial concentration of Ag^+ for a given conversion can be calculated using eqn. 3.

$$M_{Ag^+}\text{ (initial)} = \left(\frac{M_{H^+}}{K} \times \frac{\%\text{ Ag resin}}{\%\text{ H resin}}\right) + \frac{\text{mequiv. of silver on resin}}{\text{volume of solution}} \tag{3}$$

The following example illustrates the use of eqn. 3 in performing an equilibrium conversion:

A 25-ml volume of Aminex A-7 (H^+) is to be converted to the 75% silver form. The capacity of this 8% cross-linked resin is 1.7 mequiv./ml resulting in a total capacity of 42.5 mequiv. for the 25-ml amount. Seventy-five percent of this value, *i.e.* 31.88 mequiv., is the amount of Ag^+ that will be placed on the resin and will also be the amount of H^+ that will be displaced into the solution. Using 500 ml as the final volume, the following list of values can be tabulated: mequiv. of silver on resin, 31.88; volume of solution, 500 ml; M_{H^+} (final), 31.88/500 = 0.0638; % Ag resin, 75; % H resin, 25; K, 5.84.

Inserting these values into eqn. 3 gives the following results:

$$M_{Ag^+}\text{ (initial)} = \left(\frac{0.0638}{5.84} \times \frac{75}{25}\right) + \frac{31.88}{500} = 0.0966$$

To carry out the actual conversion, 25 ml of the resin of choice is slurried in 100 ml of deionized water and is transferred to a 500-ml erlenmeyer flask. The appropriate amount of silver nitrate is then added from a 0.4 M stock solution. The slurry is diluted to 500 ml with deionized water and a magnetic stir bar is added. From this point, the resin is protected from light with aluminum foil. Finally, the slurry is gently stirred for 30 min.

After conversion the resin slurry is transferred to a 350-ml medium porosity sintered glass büchner funnel, 250 ml at a time and the excess silver nitrate solution is drawn off with aspirator vacuum. The resin is then washed with three 200-ml portions of deionized water as in the initial step. All washings are collected and residual Ag^+ is determined by atomic absorption spectroscopy. From this determination the amount of silver retained by the resin can be checked.

Finally, the resin is reslurried in 200 ml of deionized water and is transferred into a light-tight container where it is stored until needed.

Column packing procedure

A 60-cm column is joined with a 30-cm column using a 3/8-in. tubing union and the assembly is clamped in a vertical position with the long column on the upper end. A 500-ml reservoir is attached to the upper end of the 60-cm column and a plugged 5-μm end fitting is attached to the lower 30-cm column. Next the assembly is filled to the bottom of the reservoir with degassed deionized water. The assembly is tapped during this step to insure that no air bubbles stick to the walls of the tubing. The prepared resin is reslurried in 200 ml of water and is transferred into the reservoir. The resin is then allowed to settle into the assembly for at least 4 h. After settling is complete the reservoir is removed and the upper end of the assembly is connected to an undamped Milton-Roy pump. Next the plug is removed from the lower end fitting and flow from the pump is initiated at a rate appropriate for the resin being packed. Pumping schedules for the various resins are listed in Table I. After packing is complete the pump is shut off and the upper column is removed from the assembly. The union is removed from the lower column and the resin from it is transferred into an end fitting. A small amount of water is added to the resin to settle it into the end fitting. The water is then removed from the resin by applying suction to the outlet of the fitting. The fitting so prepared is attached to the column and will be used as the inlet.

TABLE I

COLUMN PACKING PUMPING SCHEDULE

Time (min)	*Cross-linking (%)*					
	4 (10–15 μm)		*5–6 (10–15 μm)*		*8 (7–11 μm)*	
	Flow-rate (ml/min)	*Pressure (p.s.i.g.)*	*Flow-rate (ml/min)*	*Pressure (p.s.i.g.)*	*Flow-rate (ml/min)*	*Pressure (p.s.i.g.)*
0– 60	0.1	0– 80	0.5	0–300	0.5	0– 500
60–120	0.2	80–400*	1.0	300–600*	1.0	500–1000
120–180	—	—	—	—	1.5	1000–1500*

* Packing is stopped and the column is capped if pressure exceeds this value.

Sample preparation

Since salts, acids, soluble protein and particulate matter interfere with the quantitative analysis of corn syrups they must be removed prior to analysis. Simplified clean-up procedures for corn syrup samples have been described in a previous paper[2].

Chromatographic conditions

Unless otherwise specified the following conditions were used throughout. Solvent, deionized, degassed water maintained at 95°C; column dimensions, 30 cm × 7.8 mm I.D.; column temperature, 85°C; detector temperature, 45°C; detector attenuation, 8 ×; recorder sensitivity, 100 mV full scale; sample concentration, 2–5% dry solids basis; sample volume, 5–15 μl.

RESULTS AND DISCUSSION

Shown in Fig. 1 is the separation of a 42 D.E.* acid-hydrolyzed corn syrup on a commercially prepared 4% cross-linked resin (Ca^{2+}) run at various flow-rates. The chromatograms in the figure are typical for corn syrups separated on this support. As Fig. 1 illustrates, marked decreases in resolution occur after the DP 3, DP 6 and DP 9 regions. In addition to losses in resolution due to the structure of the corn-derived oligosaccharides, Fig. 1A–C also illustrates the loss in resolution due to increases in flow-rate. In terms of theoretical plates, the values based on the dextrose peak are 3611 for the 72-min separation, 2958 for the 36-min separation and 1738 for the 18-min separation.

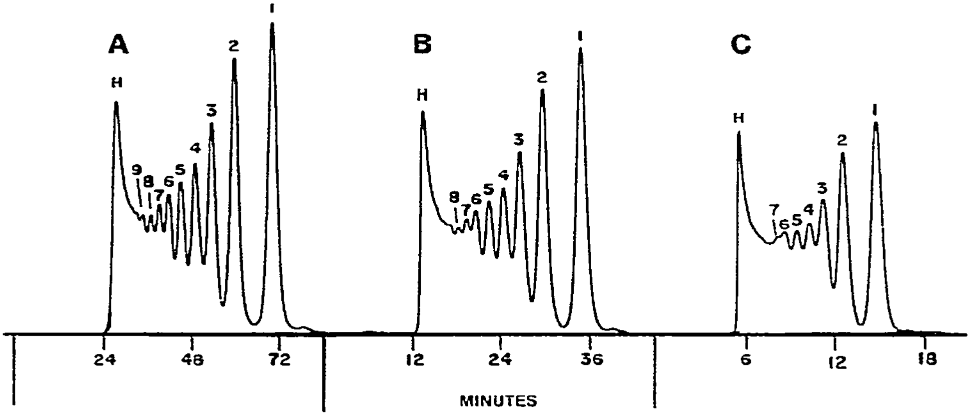

Fig. 1. Chromatograms of a 42 D.E. acid-hydrolyzed corn syrup at various flow-rates. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Aminex HPX-42 (Ca^{2+}), 4% cross-linked resin (20–30 μm). Flow-rate, (A) 0.15 ml/min; (B) 0.30 ml/min; (C) 0.60 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

These problems, along with considerable lot-to-lot variation in the compressibility of 4% cross-linked resins, prompted the continued study of silver form resins.

Shown in Fig. 2 is the separation of a 42 D.E. acid-hydrolyzed corn syrup on a 4% cross-linked resin, Aminex 50W-X4 (Ag^+) (20–30 μm). This column, described in an earlier study[2] indicated that almost twice as many oligosaccharides could be separated on a 4% cross-linked resin in the silver form than could be separated on the same resin in the calcium form. However, the resolution of the oligosaccharides on these early silver form columns, while different in character, was in general no better than that obtained on the calcium form of the same resin.

Initially it was believed that these resins were being completely converted to the silver form. However, subsequent preparations of the same resin under slightly different conditions gave considerably different results in terms of the number of oligosaccharides separated and the resolution of the separation itself. These variations in the chromatographic behavior of early silver form resins finally lead to the discovery that they were only partially loaded with Ag^+, with the remainder of the resin being

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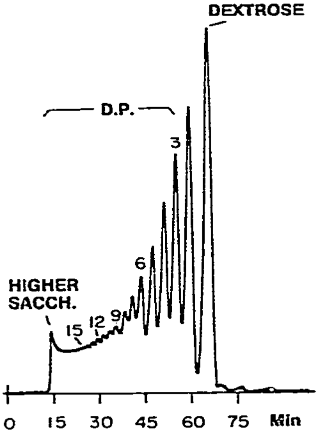
* Throughout this article, D.E. (dextrose equivalent) is defined as a measure of reducing power using a modified Lane and Eynon procedure[6].



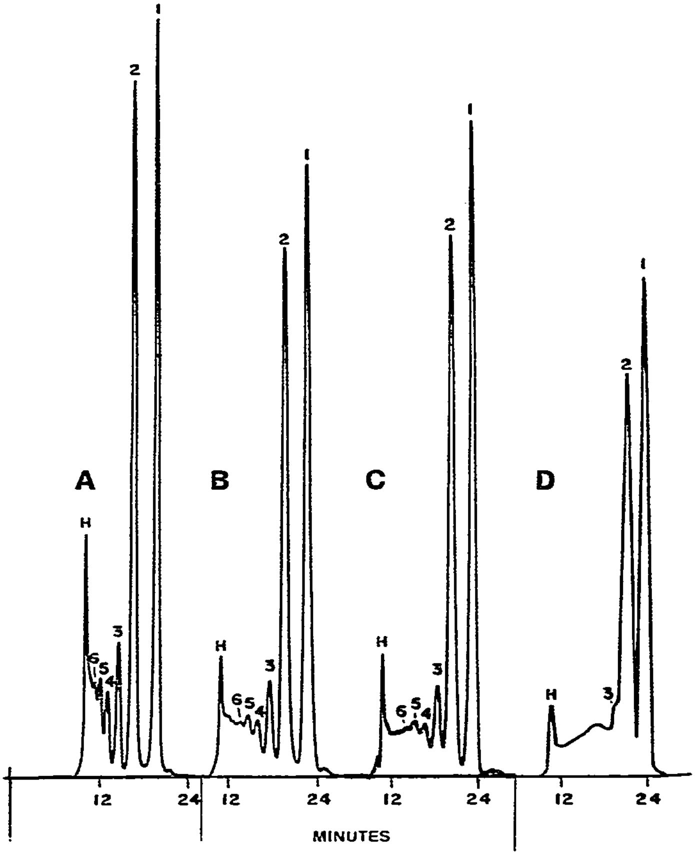


Fig. 2. Chromatogram of a 42 D.E. acid-hydrolyzed corn syrup. Chromatographic conditions: column (60 cm × 7.8 mm I.D.) Aminex 50W-X4 (Ag^+) 4% cross-linked resin (20–30 μm). Flow-rate, 0.3 ml/min. Numbers over peaks indicate DP.

Fig. 3. Effect of silver loading on resolution. Chromatograms of a 62 D.E. enzyme-hydrolyzed corn syrup chromatographed on columns with various amounts of silver loading. Chromatographic conditions: all columns (30 cm × 7.8 mm I.D.) Aminex Q-15S (19–25 μm) with (A) 70% silver form; (B) 85% silver form; (C) 95% silver form; (D) 100% silver form resin. Flow-rate, 0.4 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

in the hydrogen form. As a result of this finding, a study was conducted to determine the effect of percentage silver loading on the separation of oligosaccharides.

Separation of oligosaccharides on 8% cross-linked resins

Shown in Fig. 3 are the chromatographic results of a study in which an 8% cross-linked resin, Aminex Q-15S (19–25 μm) was converted to various silver loading levels with silver nitrate. In the calcium form this resin separates a number of monosaccharides, maltose, and maltotriose from the higher oligosaccharides. However, we found the separation of the oligosaccharides on this resin could be extended beyond maltohexaose by increasing the silver loading level to about 80%. It was noted that while increased silver loading effectively increases the retention of the oligosaccharides, it also, beyond a certain level, causes a marked reduction in the resolution of the separation. From this study it was determined more highly cross-linked resins could be used to separate oligosaccharides with more efficiency than the 4% calcium form resins, providing that the amount of silver on the resin was adjusted to an optimum level.

Shown in Fig. 4 are improved separations of a 62 D.E. enzyme-converted syrup on another 8% cross-linked resin, Aminex A-7 (7–11 μm) at the 75% silver loading level at various flow-rates. By using this high-performance resin converted to its optimum silver loading level of 75%, high resolution separation of the oligosaccharides can be obtained through DP 6 in 20 min. By increasing the flow-rate two-fold to 0.8 ml/min, the time of the analysis can be further reduced to 10 min. At this flow-rate the only peak to suffer a significant loss in resolution is the DP 6 peak. This excellent retention of resolution with increases in flow-rate is due to two additional beneficial features of silver form resins. First, silver form resins are more efficient, in terms of theoretical plates, than the same resin in the calcium form. Second, silver form resins retain their efficiency to a greater extent with increases in flow, than the

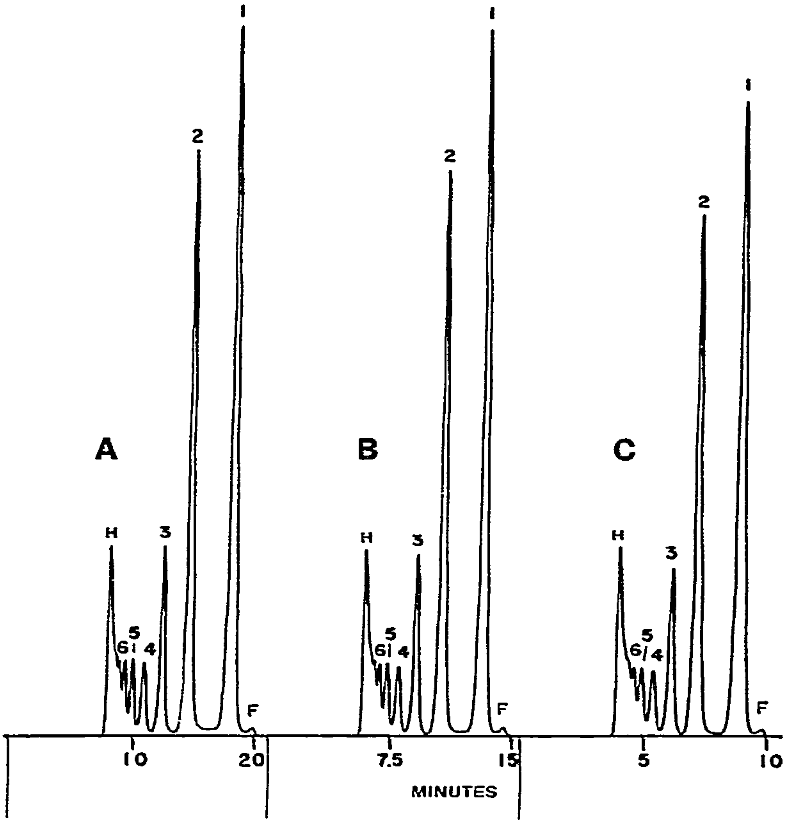


Fig. 4. Chromatograms of a 62 D.E. enzyme-converted corn syrup at various flow-rates. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Aminex A-7 (7–11 μm), 75% silver form. Flow-rate, (A) 0.40 ml/min; (B) 0.60 ml/min; (C) 0.80 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

TABLE II

CAPACITY FACTORS (*k*′) OF CORN-DERIVED OLIGOSACCHARIDES ON VARIOUS RESINS

Resin	*Counter-ion*	*Loading level (%)*	*DP*														
			1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
Aminex A-7	Ca^{2+}	100	0.63	0.33	0.21												
Aminex A-7	Ag^{+}	75	1.25	0.82	0.55	0.37	0.25	0.17	0.12								
HC-40	Ca^{2+}	100	1.18	0.82	0.61	0.46	0.35	0.26	0.21								
Aminex HPX-42	Ca^{2+}	100	1.65	1.25	1.01	0.85	0.70	0.56	0.47	0.39							
Aminex 6% X	Ag^{+}	86	1.54	1.19	0.94	0.75	0.58	0.45	0.36	0.28	0.21						
HC-40	Ag^{+}	71	2.09	1.69	1.40	1.16	0.94	0.77	0.64	0.52	0.42	0.34	0.28	0.22			
Aminex HPX-42	Ag^{+}	70	2.17	1.84	1.57	1.36	1.15	0.96	0.81	0.69	0.59	0.50	0.43	0.36	0.31	0.27	0.22

same resins in the calcium form. Fig. 5 illustrates the comparison of Aminex A-7 in both the silver and the calcium form *versus* flow-rate. At a flow-rate of 0.4 ml/min Aminex A-7 (Ag^+) is more than five times as efficient as Aminex A-7 (Ca^{2+}). Moreover, at an increased flow-rate of 0.8 ml/min Aminex A-7 (Ag^+) is more than ten times as efficient as Aminex A-7 (Ca^{2+}). These features are again due to the unique complex that silver forms with the oligosaccharides.

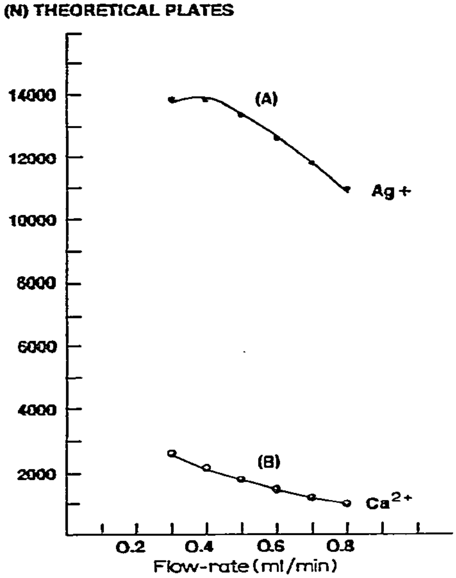


Fig. 5. Comparison of efficiency of Aminex A-7 (Ag^+) and Aminex A-7 (Ca^{2+}) *versus* flow-rate. Efficiency *versus* flow for (A) (30 cm × 7.8 mm I.D.) Aminex A-7 8% cross-linked resin column (7–11 μm), 75% silver form and (B) (30 cm × 7.8 mm I.D.) Aminex A-7 8% cross-linked resin column (7–11 μm), 100% calcium form. Theoretical plate calculations based on $N = 5.554 (t_R/W_{1/2})^2$ for dextrose, where N = number of theoretical plates, t_R = retention time, and $W_{1/2}$ = peak width at half-height.

It has been reported by Goulding[7] that Ag^+ resins form strong monodentate complexes with most monosaccharides, while Ca^{2+} forms bi- and tridentate complexes with the same series of sugars depending on their structures. While the silver monodentate complex is less selective for monosaccharides, it is much stronger than the bidentate complex of calcium for the oligosaccharides. This stronger complex brings about the greater retention of all the oligosaccharides and allows more of them to be resolved from the truly excluded higher-molecular-weight sugars. Table II lists the capacity factors of the corn-derived oligosaccharides on various resins in both the silver and calcium form.

It was also reported by the same author[7] that Ag^+ resins have little or no ability to resolve α and β anomers of glucose, while Ca^{2+} resins at ambient temperature give partial separation of the same pair. While this feature of calcium form resins is less than desirable for most purposes, it can be suppressed by operating at elevated temperature. However, since Ag^+ resins show no tendency to separate α and β anomers of the glucose oligosaccharides, operation at elevated temperatures gives rise to significantly narrower peaks than those obtained on the calcium form. This reduction in peak width along with increased retention accounts for the large differences in efficiency observed between the silver and calcium forms.

Separation of oligosaccharides on a 6% cross-linked resin

While additional oligosaccharides can be resolved from the higher excluded saccharides on 8% cross-linked resins by increasing the amount of silver on the resin, it generally results in some loss in resolution on the lower-molecular-weight end of the separation. An alternate method to increase the number of saccharides resolved is to use a resin with less cross-linking. Shown in Fig. 6 is a 42 D.E. acid-hydrolyzed syrup separated on a 6% cross-linked resin in the silver form at various flow-rates. The resin used in this portion of the study is currently an experimental 10–15-μm product with a capacity of 1.6 mequiv./ml. As illustrated in Fig. 6, this resin can separate the oligosaccharides through DP 9 when converted to 86% of its capacity with Ag^+. Also apparent is again the excellent retention of resolution with increased flow. This resin, which is only slightly less rigid than the 8% cross-linked Aminex resins, can be pumped at flow-rates of 0.8 ml/min in a 30 cm × 7.8 mm I.D. column and produce separations of the oligosaccharides in a corn syrup through DP 7 in less than 12 min. At this flow-rate the only significant loss in resolution occurs around the DP 8 region. However, in order to counteract this loss, a flow-rate of 0.6 ml/min is used and the samples are injected on an over-lap basis every 12 min with an autosampler of our own design.

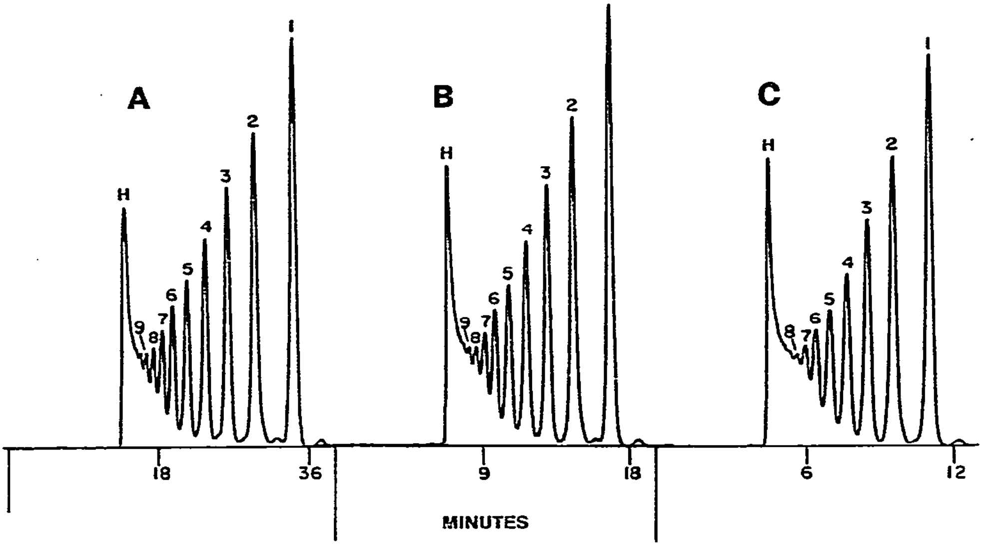


Fig. 6. Chromatograms of a 42 D.E. acid-hydrolyzed corn syrup at various flow-rates. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Aminex experimental 6% cross-linked resin (10–15 μm), 86% silver form. Flow-rate, (A) 0.25 ml/min; (B) 0.55 ml/min; (C) 0.80 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

Fig. 7 illustrates the analysis of a series of different corn syrups using the overlap injection technique. As illustrated in this figure, operation at a flow-rate of 0.6 ml/min offers the resolution of an 18-min analysis but with a sampling rate of one sample per 12 min, utilizing the relatively large void time of resin columns.

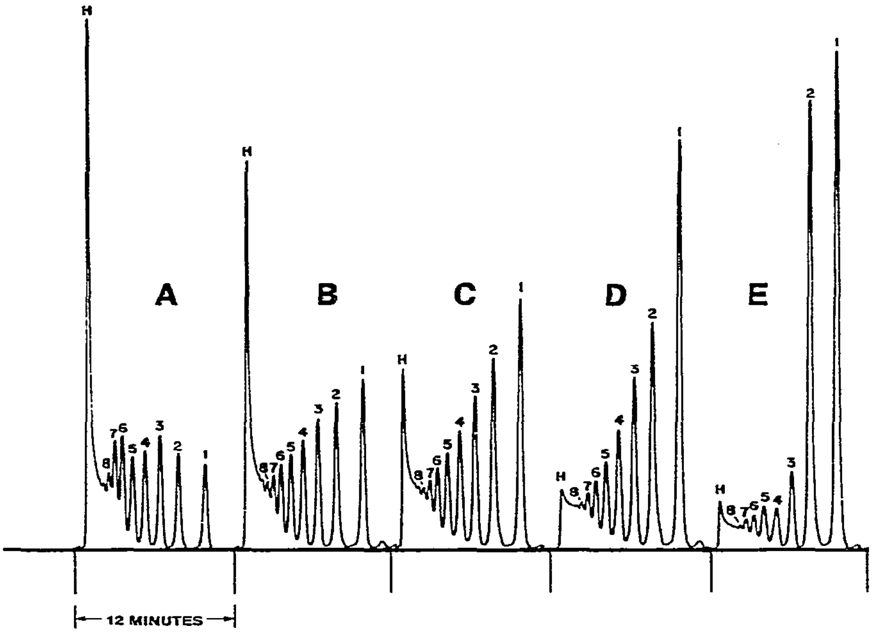


Fig. 7. Chromatograms of various corn syrups injected on an overlap basis. (A) a 28 D.E. enzyme-converted corn syrup; (B) a 35 D.E. acid-hydrolyzed corn syrup; (C) a 42 D.E. acid-hydrolyzed corn syrup; (D) a 53 D.E. acid-hydrolyzed corn syrup; (E) a 62 D.E. enzyme-converted corn syrup. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Aminex experimental 6% cross-linked resin (10–15 μm) 86% silver form. Flow-rate, 0.6 ml/min. Numbers over peaks indicate DP; H indicates higher excluded saccharides.

Although not originally intended for monosaccharide separations the high-performance silver form resins also give a satisfactory separation of fructose from dextrose. Shown in Fig. 8 is the separation of a series of saccharide standards with fructose included. While the amount of separation is not as large as that obtained on the calcium form, it is sufficient for the analysis of high fructose/regular corn syrup blends.

Separation of oligosaccharides on 4–5% cross-linked resins

While rapid separations through DP 8 are generally satisfactory for the routine characterization of corn syrups, occasionally a need arises that requires extended separations beyond this range. In an effort to fill this need, several 4–5% cross-linked resins were studied in the silver form, using the optimum loading technique.

Shown in Fig. 9 is the separation of a 42 D.E. acid-hydrolyzed corn syrup on a 5% cross-linked resin in the silver form at various flows. Although the manufacturers' original specification for this product stated that its degree of cross-linking was 4%, its mechanical strength along with its chromatographic behavior in both the silver and calcium forms indicate that it has an effective cross-linking of approximately 5%. As illustrated in Fig. 9A this resin can separate the oligosaccharides through DP 12 when converted to 71% of its capacity with Ag^+. Capable of withstanding flow-rates of over 0.6 ml/min it can produce separations of the oligosaccharides up through DP 10 when pumped at a rate of 0.7 ml/min as illustrated in Fig. 9C. However, since this

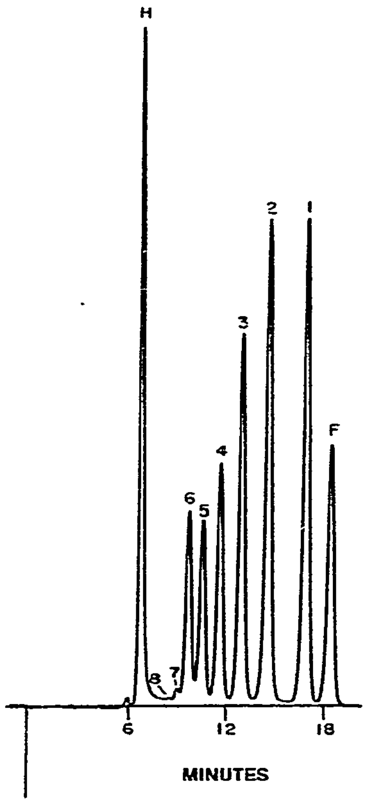


Fig. 8. Chromatogram of saccharide standards on (30 cm × 7.8 mm I.D.) Aminex experimental 6% cross-linked resin (10–15 μm) 86% silver form. Flow-rate, 0.55 ml/min. F = fructose; 1 = dextrose; 2 = maltose; 3 = maltotriose; 4 = maltotetraose; 5 = maltopentaose; 6 = maltohexaose; 7 = maltoheptaose; 8 = maltooctaose; H = dextran 10.

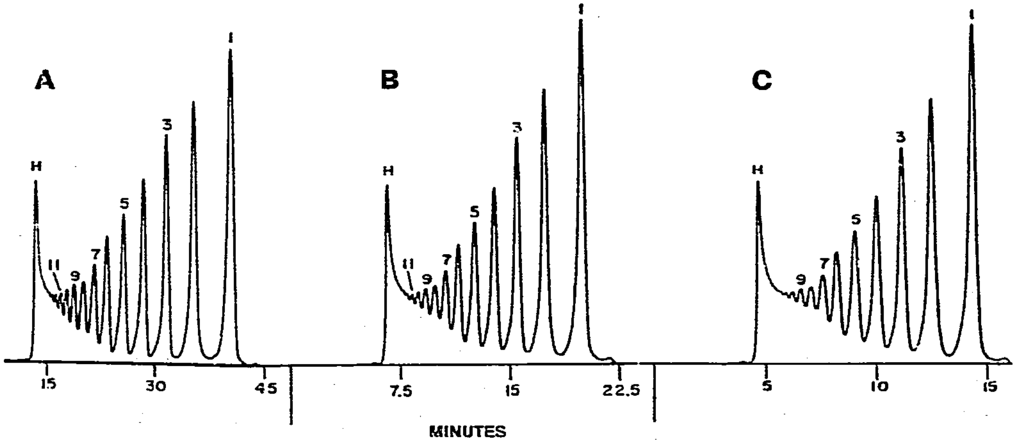


Fig. 9. Chromatograms of a 42 D.E. acid-hydrolyzed corn syrup at various flow-rates. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Hamilton HC-40 5% cross-linked resin (10–15 μm) 71% silver form. Flow-rate (A) 0.25 ml/min; (B) 0.55 ml/min; (C) 0.70 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

resin loses considerable resolution at this rate, due to a slightly asymmetrical particle size distribution, it is generally operated at the 0.55 ml/min rate shown in Fig. 9B and is injected on an over-lap basis every 18 min.

The final resin studied in this series is another experimental product designated Aminex HPX-42 (10–15 μm). This product is a smaller particle size version of the 4% cross-linked resin shown in Fig. 1. Shown in Fig. 10 is the separation of a 62 D.E. enzyme-converted corn syrup on Aminex HPX-42 (10–15 μm) converted to 70% of its capacity with Ag^+. As illustrated, this high-performance resin can separate oligosaccharides through DP 15 in 60 min when operated at a flow-rate of 0.2 ml/min. Shorter analysis times are not practical with this resin since its small particle size gives rise to critically high backpressure at flow-rates above this value. While this column does not operate at the higher speeds of the other columns shown, it does illustrate that with optimum silver loading, high-resolution separation of corn-derived oligosaccharides can be made through DP 12 without marked losses in resolution after every half turn of the helix.

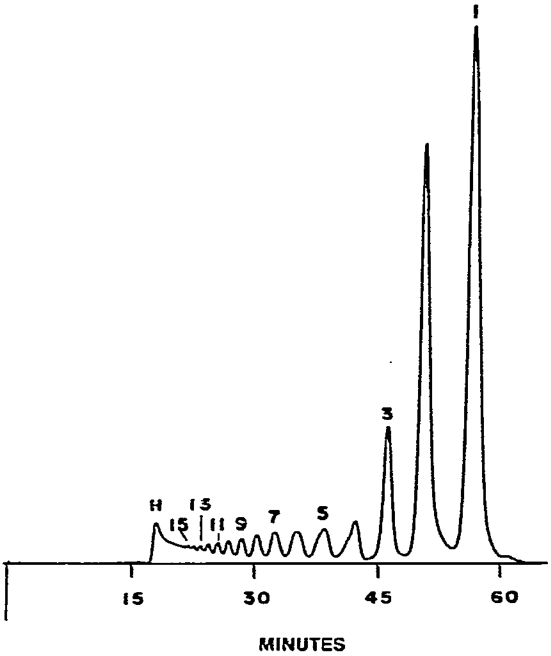


Fig. 10. Chromatogram of a 62 D.E.. enzyme-hydrolyzed corn syrup. Chromatographic conditions: column (30 cm × 7.8 mm I.D.) Aminex 4% cross-linked resin (10–15 μm) 70% silver form. Flow-rate, 0.2 ml/min. Numbers over peaks indicate DP; H indicates higher excluded oligosaccharides.

CONCLUSION

We have found that the increased retention and resolution characteristics of silver form resins provide an analysis of corn derived oligosaccharides superior to that obtained on equivalent resins in the calcium form. While the aspect of partial silver loading is not yet clearly understood, it has provided a method to produce high-resolution separations of oligosaccharides on mechanically stable resins that in other metallic forms resolve only mono-, di- and trisaccharides. Partial loading also appears to increase column life of silver form resins. Several columns from this study have been in operation for over 22 months and they show no indication of silver reduction.

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