

NON-SUGAR REMOVAL IN THE MOLASSES AND RAW JUICE
CHROMATOGRAPHIC SEPARATION PROCESSES (ASSBT 1995)

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The Amalgamated Sugar Company has been involved for years in the application of ion exclusion chromatography to the enhanced recovery of sucrose from sugarbeet process streams. Laboratory-scale tests of a simulated moving bed chromatography system for sucrose recovery from sugarbeet molasses were initiated in August 1981 and pilot scale tests were begun shortly thereafter. The technology developed in this continuing project led to construction and start-up of the world's first process-scale simulated moving bed chromatography system for molasses treatment at the Hokkaido Sugar Company's Kitami Factory in 1985 and the first such U.S. system at Amalgamated's Twin Falls factory in 1988. Continuing research on ion exclusion applications in sugarbeet molasses treatment has led to the licensing of other systems in Europe and the United States. Most recently, interest has been directed to the purification of diffusion juice directly by ion exclusion¹.

Much information on the elimination of various non-sugars has been collected during research on the application of ion exclusion technology to the purification of sugarbeet process streams. Non-sugar elimination data for both molasses and diffusion juice will be discussed in this paper, with particular emphasis on the differences between ion exclusion purification and conventional juice purification. It should be kept in mind that non-sugar elimination is dependent to some extent on the particular operating conditions of the system but the following discussion will give an idea of the general applicability of ion exclusion to removal of various non-sugars. All molasses data given in the following description is based on analysis of composite samples from a factory-scale system (Twin Falls factory) and diffusion juice data is based on pilot tests.

Although the separation process is designated as an ion exclusion separation, in the course of this study examples of several different separation mechanisms were encountered. These include:

(1) Ion exclusion separation which takes advantage of the fact that charged species (cations and anions) diffuse into the ionic matrix of ion exchange resin beads with more

¹ "The Amalgamated Sugar Company raw juice chromatography separation process", M. Kearney, V. Kochergin, K. Petersen, L. Velasquez and B. Jacob; paper presented at A.S.S.B.T. 28th General Meeting, March, 1995.

difficulty than small neutral molecules such as disaccharides and monosaccharides.

(2) Size exclusion reflects the lower rate of diffusion of large molecules into the small pores of the resin matrix. Size exclusion allows the separation of neutral molecules, such as carbohydrates, of various sizes.

As might be expected, these effects can both operate in varying degrees depending on the size and ionic nature of the species under consideration.

RESULTS AND DISCUSSION

I. Molasses Non-Sugars

A. Ionic Constituents

Total inorganic constituents, as measured by an ashing technique are very efficiently removed by ion exclusion chromatography. In typical factory composites, 94-98% of ash constituents in molasses are removed in the by-product, or raffinate, stream. The sucrose-containing stream, or extract, is thus quite low in inorganic salts and sugar boiled directly from extract is typically low in ash.

Of the individual inorganic compounds measured in separator streams, the most easily removed are the common inorganic anions (sulfate, chloride, nitrate, nitrite, sulfite, and phosphate). These species, being strongly ionized and negatively charged (like the polymeric matrix of the cation exchange separation medium), are very efficiently excluded from the resin matrix. Typical measured elimination values for inorganic anions, as determined by ion chromatographic analysis of factory streams, is 99% or higher.

The only simple organic acid anions studied to date are malate and oxalate. Malate seems to be eliminated at as high a level (99.4%) as inorganic anions. Oxalate removal has been measured as 98.6% although levels are low enough in molasses to make a material balance determination uncertain.

Removal of inorganic cations in the separator is slightly less efficient than that of inorganic anions. Typical removals, measured by atomic absorption spectrophotometric analysis of process streams, are 94-98% for potassium and sodium. The reason for the apparent difference between elimination values for inorganic anions and cations is not known for certain but a very likely possibility relates to the presence of organic anions in molasses solutions. Inorganic anions, such as chloride and sulfate, are strongly excluded from the cation exchange resin and, to maintain charge balance, must carry an equal number of cations with them. However, a small but significant fraction of inorganic cations are associated with organic anions, such as the anionic forms of amino acids. If such salts have potassium or sodium ions tightly associated with the anion the ion pair might be speculated to behave slightly more like a neutral

compound and be retarded in travel through the resin bed. Thus any cations involved in such salts would lower the overall elimination of monovalent cations from the level expected for strongly ionized inorganic salts.

B. Nitrogen Compounds

Nitrogen-containing components of sugarbeet molasses vary widely in ease of elimination by ion exclusion treatment. Based on analysis of factory composites, nitrogen compounds as a class (determined by total nitrogen determination) are approximately 80% eliminated across the separator. However, within this group, separation characteristics vary widely depending on chemical properties and some of the more poorly-removed compounds are within the group.

Ammonia is not present at high levels in molasses and the small amounts measured in separator feed may even come from condensate used for dilution. Ammonia present in separator feed appears to be approximately 85% removed in ion exclusion, which is not surprising if most ammonia is considered to be present as ammonium ion.

Nitrogen compounds containing the α -amino nitrogen functional group, such as amino acids, are removed to the extent of 60-80% as a class, depending on separation conditions. However, removal of individual compounds within the amino acid class varies drastically and will be the subject of a future report.

One of the major nitrogen compounds in sugarbeet molasses, betaine, is present at typical levels of 6-7% based on dissolved solids and is the major molasses component that is most difficult to remove by ion exclusion. Typical betaine removal with raffinose, under factory operating conditions, is 65% of the betaine entering. A combination of the high level of betaine in molasses and the relatively low removal results in betaine being the major non-sugar in separator extract, at a level of 40-60% based on non-sugars.

C. Carbohydrates

As neutral molecules, carbohydrates are not subject to separation by an ion exclusion mechanism. The common carbohydrates present in factory streams, furthermore, are significantly different only in molecular weight. The fundamental mechanism for carbohydrate separation during treatment of process streams is therefore probably size exclusion, or the tendency of large molecules to be excluded from the small pores of the ion exchange resin matrix.

The inversion products, fructose and glucose, as monosaccharides, would be expected to diffuse more easily than sucrose into the separation medium. Thus monosaccharides would be expected to elute after sucrose in a separation profile. Due to the cyclic nature of the separation

in a simulated moving bed system any material which lags behind in the separation profile can actually become part of material removed, at the leading edge of the profile, with raffinate. (This behavior can be thought of as analogous to a slow racer who lags behind and is "lapped" or caught up with by the main group). Invert is present in such low quantities in sugarbeet molasses that balance data may vary but typically over 60% of invert is removed in raffinate.

Raffinose is a significant component of most sugarbeet molasses and, as a trisaccharide, would be expected to have a lower tendency to diffuse into the resin matrix than sucrose and thus should move ahead of sucrose in the separation profile. Raffinose is typically removed with about 80% efficiency in factory-scale chromatography systems.

Polysaccharides, having high molecular weights, are expected to be much different than sucrose in rate of diffusion into the separation medium. Large molecules like polysaccharides should be effectively excluded from resin pores and thus move ahead of lower molecular weight saccharides. Data to verify this with dextran was collected during the 1991-92 campaign when the Twin Falls factory processed frost-damaged beets. Molasses produced during this period was high in dextran, as measured by the Roberts method, but other than a slowing of the feed molasses filtration step no problems were experienced with the separation system. Sample collection and dextran determination showed that molasses containing 2600 ppm dextran (solids basis) was processed to give sucrose-containing extract with less than 50 ppm dextran and raffinate containing 7900 ppm dextran. A material balance calculation indicates that 99% of dextran entering the separation system is eliminated in raffinate. Thus the ion exclusion sucrose recovery system also performs as a very efficient dextran removal step.

II. Non-sugar removal in raw juice treatment by ion exclusion chromatography

The application of ion exclusion chromatography to the purification of concentrated raw juice has been of recent interest at Amalgamated Sugar and is the subject of another paper at this meeting¹. Non-sugars in raw juice behave similarly to those in molasses with respect to removal by chromatography. The use of chromatographic technology as the primary purification process for raw juice invites a comparison with the present method of juice purification, liming and carbonation. Table 1 shows values for removal of various non-sugars from raw juice by ion exclusion chromatography, based on preliminary pilot tests, versus approximate removal values by liming and carbonation. Non-sugars are grouped by their customary designation as "removable" or "non-removable" by liming and carbonation.

TABLE 1
Removal of Raw Juice Non-Sugars

| | Liming and Carbonation | Chromatographic Separation |
|-----------------------------|------------------------|----------------------------|
| Removable Non-Sugars | | |
| Phosphate (%) | 95 | 97 |
| Sulfate (%) | 35 | 99 |

| | | |
|---------------------------------|----|-----|
| Oxalate (%) | 99 | 91 |
| Malate (%) | 80 | 90 |
| Invert (%) | * | 37 |
| Non-Removable Non-Sugars | | |
| Potassium (%) | 0 | 95 |
| Chloride (%) | 0 | 99 |
| Nitrate (%) | 0 | 94 |
| Raffinose (%) | 0 | 27 |
| Betaine (%) | 0 | 32 |
| Amino Acids (total) (%) | 0 | ~30 |

* Invert is destroyed in liming and carbonation but resulting non-sugars (such as lactate) may still be present.

As shown by the data in Table 1 most non-sugars, other than oxalate, are removed at higher levels by ion exclusion separation than by liming and carbonation. Among the non-sugars "removable" by conventional juice purification, differences are not extreme except for sulfate. Oxalate, due to the extreme insolubility of the calcium salt, is removed more efficiently with liming while in ion exclusion separation it behaves as any other anion. Invert is somewhat of an exception to the removal data since it is not actually removed from solution during liming and carbonation but merely converted to less troublesome non-sugars, such as lactate, which stay in the juice stream. The separation process, on the other hand, does not destroy invert but physically removes over one-third of it.

The major difference between conventional juice purification and ion exclusion chromatography is in the behavior of what are usually referred to as "non-removable" non-sugars. In particular, the soluble inorganic anions and monovalent cations, which go straight through liming and carbonation, are removed very efficiently in the separation system. The less efficiently removed more weakly ionic materials, raffinose, betaine, and amino acids are also at least partly removed by ion exclusion separation. No information was gathered on organic acids with soluble calcium salts (lactate, acetate) but it is expected that removal of these anions would be similar to other organic acids. In summary, the data of Table 1 shows that most non-sugars, including those not removed by liming and carbonation, can be removed more thoroughly by ion exclusion chromatography.

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