The Composition of Beet Molasses with Particular Reference to Nitrogenous Compounds

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Introduction

In the United States two principal types of beet molasses are produced—straight house and Steffen molasses. Molasses from a straight house is the mother liquor remaining after the economical crystallization of sugar from purified and concentrated sugar beet extracts. In the Steffen process, straight house molasses is treated with calcium oxide to precipitate a calcium complex of sucrose; most of the impurities remain in solution. The precipitate is recycled to the carbonator to recover the sugar and provide a source of lime. Molasses formed after this secondary crystallization of the sugar is Steffen molasses.

A comparative study of Steffen and straight house molasses composition is necessary to determine the most economical use of molasses, as well as being a valuable adjunct to other processing investigations, such as the effect of molasses composition on sugar crystallization. Samples of molasses representative of the various beet processing areas of the United States were furnished by the beet sugar companies and were analyzed at this Laboratory for a number of their chemical constituents. The results of these analyses and additional data obtained in earlier work from this Laboratory are presented in this paper.

Results and Discussion

In Table 1 a comparison is made between Steffen and straight house molasses. High, low, and average values are presented to provide an estimate of the composition extremes as well as the mean values. The averages represent 18 straight house and 13 Steffen samples. The data in the remainder of the tables are from a small number of different samples from various sources. No distinction was made between straight house and Steffen molasses in these tables, since the variation between samples of one kind of molasses is much greater than the difference between the two types.

True purity values (sucrose as a percent of total solids) are presented in Table 1. Sugars, after inversion with invertase,

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Table 1.—Composition of straight house and Steffen beet molasses.

		High	Low	Average
		Percent sucrose on solids		
Purity	Straight house	67.4	59.1	63.2
	Steffen	65.7	61.2	63.4
		Grams/100 g of non-sucrose solids		
Sucrose	Straight house	207.0	144.4	171.4
	Steffen	191.9	157.9	173.1
Reducing substances	Straight house	7.8	1.0	2.0
	Steffen	3.7	0.9	1.6
Raffinose	Straight house	8.4	0.7	3.1
	Steffen	10.9	3.0	6.0
Potassium	Straight house	19.8	11.2	14.4
	Steffen	16.3	8.4	12.0
Sodium	Straight house	6.7	1.4	3.5
	Steffen	6.2	1.4	3.6
Chloride	Straight house	6.6	0.7	3.5
	Steffen	5.8	1.3	3.0
Nitrate	Straight house	3.7	1.1	2.4
	Steffen	3.1	1.3	2.3
Total nitrogen	Straight house	7.0	4.2	6.2
	Steffen	6.5	4.1	5.3
Betaine	Straight house	19.2	10.2	15.4
	Steffen	14.3	9.7	12.6
Amino Acids[1]	Straight house	12.6	6.6	9.6
	Steffen	10.8	6.6	8.5
Amides[2]	Straight house	1.4	0.2	0.8
	Steffen	1.2	0.1	0.7
Anions[3]	Straight house	48.5	40.9	43.4
	Steffen	48.3	38.5	42.9
Anions (Milli-equivalents)[3]	Straight house	573.0	403.0	490.0
	Steffen	497.0	424.0	458.0
Anions (Avg eq. weight)[3]	Straight house	104.5	74.5	89.2
	Steffen	106.1	83.1	93.8

[1] Amino nitrogen times 8.4.
[2] Amide nitrogen as asparagine.
[3] Amphoteric compounds (amino acids, etc.) not included.

were determined chemically by the Munson-Walker method. Solids were determined by vacuum-oven drying. There is little difference in the average purity of the two types of molasses. It must be remembered, however, that more sugar is recovered from the beets by the operation of the Steffen process and less total molasses is produced. Since the ratio of sugar to non-sugar is higher in high purity molasses it is obvious that there is more sugar lost to molasses per unit weight of non-sucrose solids in the high purity samples, although the particular factory concerned may produce less total molasses per ton of beets if it is processing high purity beets. The magnitude of the sugar loss in high purity molasses is emphasized by the weight of sucrose in molasses per 100 grams of non-sucrose solids (Table 1). The highest purity straight house molasses shows a 20% greater loss of sucrose into molasses than the average. Expressing the results on a tonnage basis, the highest purity molasses carries 34 tons more sugar into molasses for every 100 tons of non-sugar solids than the average. Viewed in a different manner, a factory producing average molasses would bag 34 tons more sugar per 100 tons of non-sucrose solids than the factory producing the highest purity molasses.

There is considerable spread in reducing sugar values in both types of molasses. These differences may be due to variations in processing although the previous history of the beets, including extent of storage and storage temperatures, probably plays an important part.

Since raffinose, when treated with calcium oxide in a solution such as molasses, forms an insoluble calcium complex, Steffen molasses should contain more raffinose than straight house molasses. This is borne out by the results shown in Table 1. However, it is generally accepted that beets grown in the Southern California region contain the minimum and those grown in the Rocky Mountain or Kansas areas contain the maximum raffinose. This is reflected in the molasses; samples from these regions are respectively below and above average in raffinose. A study of the raffinose content of the individual Steffen molasses samples indicates that the amount of raffinose may not always be the controlling factor requiring the discard of molasses, although the decision to discard molasses in factory operations may be based in part on this value.

The two metallic ion impurities present in greatest quantity are potassium and sodium. Steffen molasses contains less potassium than straight house molasses but average about the same sodium content. The proportionate variation in sodium is much greater than for potassium. This may be due, in part, to genetic differences in soil composition, but part of it is due to the addition of sodium carbonate or sodium hydroxide to some factory juices to preserve alkalinity. The addition of sodium carbonate would also account for the similarity of sodium composition in the two types of molasses, because much more sodium carbonate is needed to preserve alkalinity in the Steffen process. Since calcium is precipitated during processing, it is present in much lower quantities, averaging 0.5 and 0.7% on non-sucrose solids for straight house and Steffen molasses, respectively. Magnesium is present in even smaller quantities.

There is a greater variation in chloride content (10 fold) than in any other major component of molasses except raffinose. This variation may be very important. We have some indications that chloride as the sodium or potassium salt is very melassigenic and that a low chloride content is associated with the production of low purity molasses. This finding indicates the desirability of removing chloride and preventing its addition to the factory juices.

A noteworthy feature is that nitrate is nearly as high in Steffen as in straight house molasses. The essence of the Steffen process is the return of sucrose in the form of a sucrose-calcium complex and of other substances forming insoluble calcium compounds to the diffusion juice, while the soluble impurities are filtered off. It would be expected that substances that do not react with calcium and those forming soluble calcium salts, such as nitrate, would appear in lesser quantities in Steffen molasses. This is true for potassium, chloride, and many other substances, but does not appear to hold true for nitrate even though calcium nitrate is very soluble in water.

The average total nitrogen content of Steffen molasses is lower than that of straight house molasses. It is possible that the total weight of nitrogen-containing compounds is also lower, although this does not necessarily follow, since the unidentified nitrogen compounds in Steffen molasses may have a lower percentage nitrogen and hence give a greater weight of compound per unit of nitrogen. The nitrogen compound present in largest amounts in molasses is betaine. Quantitatively, there is a considerable difference between the high and low values of betaine for both types of molasses. Since betaine is not precipitated by calcium ions it passes into the Steffen filtrate and its concentration is less in Steffen molasses. Similar variations are found in the amino acid and amide fractions. The weight of amino acids was calculated from the amino nitrogen content and multiplied by a factor of 8.4 to convert to amino acids. Since glutamine is degraded during processing, leaving asparagine as the principal amide in molasses, total amide nitrogen was calculated as asparagine. The amount of nitrogen present as betaine, amides, and amino acids listed in Table 1 accounts for only 50% of the total nitrogen in molasses.

There are more equivalents of anions present (about 8%) in straight house molasses than in Steffen molasses, but the average equivalent weight of the anions in straight house molasses is about 6% lower. The reason for the lower average equivalent weight of anions is due to lower equivalent weight anions forming more soluble calcium salts and being eliminated in the waste to a greater extent in the Steffen process. The actual weight of anions in the two molasses is nearly the same, 43 g/100 g of non-sucrose solids, although the composition of the anions differs materially.

Reducing substances, raffinose, potassium, sodium, chloride, nitrate, betaine, amino acids, and amides make up 55% and 51% of the non-sucrose solids of straight house and Steffen molasses, respectively. Since the total for the impurities listed in Table 1 are 4% less for Steffen molasses, some undetermined and possibly unidentified substances appear to be concentrated in Steffen molasses in a manner similar to the build-up of raffinose which is recycled through the factory as the calcium-raffinose complex.

The quantities of some of the principal anions present in molasses are presented in Table 2. It should be noted that total sulfur was calculated as sulfate, although part of the sulfur is present as sulfite or as an integral part of some organic compounds. Pyrrolidone carboxylic acid (PCA) accounts for about one third of the anions listed in Tables 1 and 2.

Table 2.—Some anions present in beet molasses.

Anion	Grams/100 g of non-sucrose solids
Lactate	4.7
Glycolate	1.4
PCA	9.4
Citrate	1.0
Malate	1.9
Sulfate[1]	4.6

[1] Total sulfur as sulfate.

Source: Owens, H. S., Stark, J. B., Goodban, A. E. and Walker, H. G. 1955. Applications of compositional knowledge to beet sugar technology. Agr. Food Chem. 3: 350-353.

Table 3.—Principal amino acids in beet molasses.

Amino acid	Grams/100 g of non-sucrose solids	Amino acid	Grams/100 g of non-sucrose solids
Alanine	0.8	Leucines	1.3
Aspartic	1.5	Serine	0.7
Gamma-aminobutyric	1.3	Threonine	0.6
Glutamic	1.5	Tyrosine	0.7
Glycine	0.4	Valine	0.6

Source: Goodban, A. E., Stark, J. B. and Owens, H. S. 1953. Amino acid content of sugar beet processing juices. Agr. Food Chem. 1: 261-264.

Table 3 shows the approximate quantity of the principal amino acids found in molasses. Other amino acids, such as tryptophane, are present in lesser quantities. The most economically important is glutamic acid which appears in the Steffen filtrate and can be converted to monosodium glutamate. The other amino acids are important, because they improve the value of beet molasses as a feed supplement or as a fermentation medium.

Table 4 gives the approximate quantities of purine, pyrimidines, and nucleosides found in molasses. If an adequate market could be found, some of these compounds might be economically recovered from beet molasses or other by-product liquors.

An arbitrary classification of nitrogen-containing compounds present in sugar beet liquors has been made on the basis of their reaction to ion exchange resins. The scheme of separation is shown in Figure 1. In this example, a dilute molasses solution is passed through a column of cation resin in the hydrogen form. Compounds retained by the resin and the nitrogen in these compounds are classed as basic even though some of them, amino acids in particular, can be adsorbed by an anion exchange resin. The effluent from the column is passed, in turn, through a column of anion resin in the formate-chloride form. The nitrogen present in the compounds adsorbed by the resins is classed as acidic. The portion not adsorbed by either resin is classed as unadsorbed. The relative amounts of these three classes are shown in Table 5. From the data in earlier tables and other work not presented in this paper, it has been found that nearly 50% of the basic nitrogen is present as betaine. Amino acids account for 25%, while amides, ammonia, and purines constitute an additional 9%. Seventeen percent remains to be identified. About 55% of the acidic nitrogen is present in PCA. Nitrate accounts for 22%, amino compounds for 5% and 18% is unidentified. Six percent was unadsorbed and has not been identified.

Table 4.—Principal purines, pyrimidines and nucleosides in beet molasses.

Compound	Grams/100 g of non-sucrose solids	Compound	Grams/100 g of non-sucrose solids
Adenine	150	Uracil	10
Guanine	100	Uridine	200
Hypoxanthine	10	Unknowns	10
Thymidine	15		

Source: Stark, J. B., Jaouni, T., and Bailey, G. 1956. The purines, pyrimidines and nucleosides in beet diffusion juice and molasses. J. Am. Soc. Sugar Beet Technol. 9: 201-206.

Table 5.—Distribution of beet molasses nitrogen.

Class	Percent
Basic	66
Acidic	28
Unadsorbed	6

Source: Stark, J. B., Goodban, A. E. and McCready, R. M. 1959. The fractionation of nitrogen compounds in beet molasses. J. Am. Soc. Sugar Beet Technol. 10: 571-577.

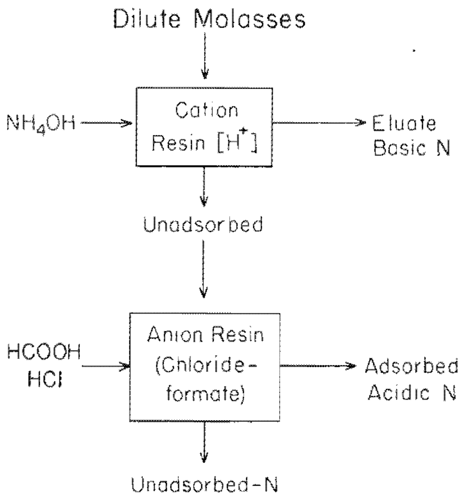

Figure 1.—Fractionation of nitrogen compounds by ion exchange resins, Dowex-50[1] and Dowex-1[1].

Summary

Differences in composition are shown for straight house and Steffen molasses. High, low and average values are shown for purity, sucrose, reducing substances, raffinose sodium, potassium, chloride, total nitrogen ,amino acids, betaine, amides, anions, milliequivalents of anions and average equivalent weight of anions. Raffinose is the only substance determined that is present in significantly greater amounts in Steffen molasses non-sucrose solids than in straight house molasses. Fifty-five percent of the impurities in straight house molasses was determined and only 51% in Steffen molasses. Some unidentified compounds besides raffinose have been concentrated in the molasses during the operation of the Steffen process.

[1] Reference to a company and/or product name by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Two thirds of the nitrogen present in compounds in molasses can be removed on a cation exchange resin. Betaine and various amino acids form most of this fraction. Most of the remaining nitrogen compounds can be adsorbed on a strongly basic anion exchange resin in the formate-chloride form.

An ion exchange procedure is described that can be used to separate a number of nitrogen compounds found in molasses.

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