well recognized. To some extent, they replace sugar in saturated solution. Therefore, Steffen molasses is produced at a purity lower than non-Steffen. But, because they increase viscosity and, in the case of raffinose, interfere with crystal development (*8*), the carbohydrate nonsucrose components decrease the crystallization rate. Specific effects of the members of the carbohydrate group, other than raffinose, have not been investigated, but there is evidence that they also replace sugar in saturated solutions of low purity.

The carbohydrate content of a liquor is the primary factor in determining its viscosity. Therefore, carbohydrate compounds may indirectly cause a depression of crystallization rates, but if the sugar end has sufficient capacity their presence will result in a reduced molasses purity.

That different liquors present different processing problems cannot be questioned. A reduction in the raffinose content of the beet would be advantageous. It is anticipated that the beet breeders will make progress in this line in the near future. But it appears that the major improvement will be made by reduction of the total nonsucrose components in the carbonated juice. With the introduction of a method for determining the purity of carbonated juice yielded by individual mother beets (*5*), it is hoped that the beet breeders will be able to provide juices containing less of all types of nonsucrose components. However, a reduction of quantity of nonsucrose compounds in the beets worked, which will reduce the quantity of molasses produced, will do little to simplify the problem of obtaining molasses of minimum purity, because it will not make the crystallization of sucrose, from low purity liquors, more rapid.

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BEET SUGAR TECHNOLOGY

Application of Compositional Knowledge to Beet Sugar Technology

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Investigations of the composition of beets and their processing liquors have been under way for about 5 years. Results of these studies and their significance in beet technology are reviewed.

Studies of the composition of sugar beets and beet-processing liquors in recent years have provided much necessary fundamental information on changes in composition effected by processing, and on the nature of melassigenic compounds and agents which have deleterious effects on processing. At this laboratory, a general study of the composition of beets and their processing liquors has been under way during the past 5 years. This paper reviews the findings and suggests what they mean to beet technology.

Marc Analysis

The sugar beet contains about 95% juice and 5% marc, the water-insoluble portion. Because only a small amount of information is available on the marc, it was analyzed in 80 different varieties of beets and found to vary from 2.7 to 6% of the weight of the beet (*2*, *13*). Of the 80 samples of marc, 15 were analyzed for anhydrouronic acid (a measure of pectin), araban, and galactan. Results are given for some of the samples in Table I. There is a positive correlation between sucrose and marc, and sucrose and araban. Anhydrouronic acid appears in almost constant percentage in the marc (*13*). No conclusions can be drawn concerning galactan because the analytical method was not sufficiently accurate. These compounds are mentioned again in the discussion on alcohol-insoluble constituents.

Preparation of Juice Samples

Cossettes were collected at four different factories located in various parts of the country. The cossettes were immediately placed in boiling 70% isopropyl alcohol. After 15 minutes' heating, the mixture was cooled and subsequently shipped to this laboratory, where the alcohol was removed by evaporation. The cossettes were then extracted three times in boiling water. The extracts were concentrated to about 10% sugar concentration.

Factory diffusion juice from similar cossettes was collected, concentrated in vacuo, and sent to this laboratory. Molasses samples were also collected, but they probably were not representative of the same beets as those sampled for cossettes and diffusion juice.

Although data were obtained on juices from these four factories and later on diffusion juice and molasses from 13 factories, for purposes of simplification only those from Moorhead, Minn., are presented. The results on juices from various factories generally disagreed in amount, but the nature of constituents

Table I. Determination of Sucrose, Marc, and Water-Soluble Polysaccharides in Beets

(% on beet)

1952 No.	Sucrose	Marc	AUA[a]	Arabinose	Galactose
81	12.6	3.8	0.95	0.46	0.2
115	9.0	2.7	0.70	0.32	0.3
188	14.6	4.1	0.90	0.62	0.2
246	15.3	6.1	1.46	1.10	0.3

[a] Anhydrouronic acid.

Table II. Amino Acids in Beet Juices and Molasses

(Moorhead, Minn. Mg./100 g. sugar)

Amino Acid	Cossette Juice	Diffusion Juice	Molasses	
			Found	Calcd.
Betaine	...	1650	10,610	9900
GABA[a]	110	95	540	570
Valine	50	40	240	240
Leucine	80	80	420	480
Alanine	60	50	320	300
Tyrosine	...	80	300	480
Serine	70	60	340	360
Aspartic	180	160	820	960
Asparagine	...	100	470	600
Glutamic	170	190	720	1140
Glutamine	(830)	<830	None	...
PCA[b]	...	Present	5010	...
Threonine	...	60	270	360
Glycine	...	20	230	120

[a] γ-Aminobutyric acid.
[b] Pyrrolidone carboxylic acid.

was essentially the same (17). The data are separated into arbitrary classes and the changes in each class of compounds are followed through some factory operations to the molasses stage.

Amino Acids

Amino acids were determined chromatographically by the two-dimensional technique (7). Betaine was determined by the method of Walker and Erlandsen (18). Glutamine was assumed to dehydrate to pyrrolidone carboxylic acid (PCA) during the boiling or concentrating stages through which the juices passed. The pyrrolidone carboxylic acid was fractionated by ion exchange technique (12) and determined by total nitrogen analysis.

Table II summarizes the results on the amino acids. By comparison with earlier results (7), it emphasizes that concentrations may differ in different factories, but that the amino acids and the changes they undergo are similar. The calculated value for the molasses is based on the assumption that the yield of molasses is about 5% of the weight of the beet, while the sugar in molasses is concentrated between three- and fourfold above its concentration in diffusion juice. Thus a value of sixfold was chosen to represent the expected increase in impurities with respect to sugar. If it is assumed that betaine and such amino acids as valine, leucine, and alanine undergo no change during processing, an average factor of approximately sixfold seems justified.

Except for glutamine, there are no significant differences among the amino acids in cossette juice as compared to diffusion juice. It is concluded that beet-cell walls are permeable to simple amino acids and no elimination of this part of the so-called "harmful" nitrogen can be achieved in the diffuser.

From diffusion juice to molasses, several changes occur. The dicarboxylic acids are decreased below the calculated value, possibly as a result of adsorption on the lime cake. Reverse aldol reaction involving threonine and serine is not so pronounced in these factory juices as in those reported earlier (7). Although some of the amino acids enter browning reactions most of them go into molasses unchanged. The main exception is glutamine, but it appears almost quantitatively as pyrrolidone carboxylic acid. Besides contributing to color formation, which increases the difficulty of making white sugar, amino acids may increase lime salts during processing, because the increase in pH

Figure 1. Buffering capacity of factory juices

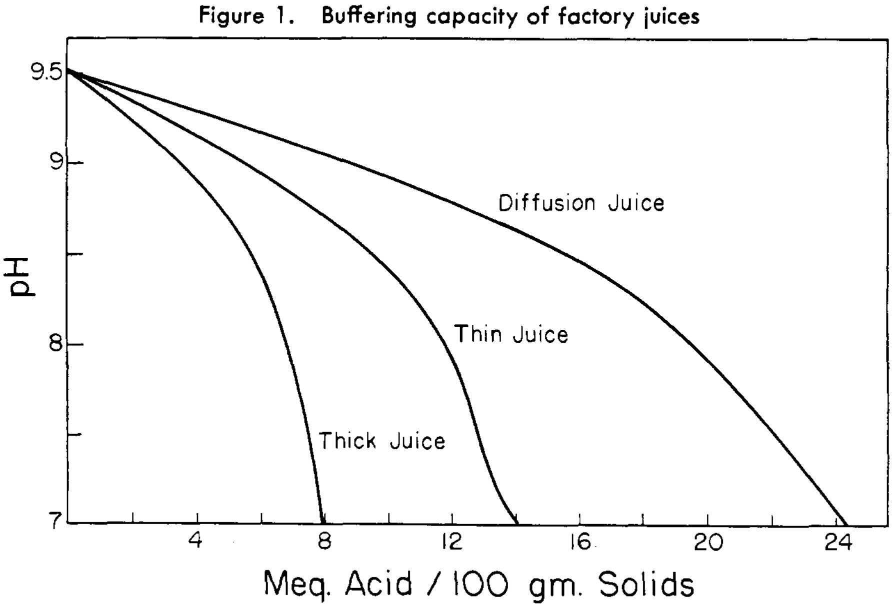

Table III. Anionic Constituents of Beet Juices and Molasses

(Moorhead, Minn. Mg./100 g. sugar)

Anion	Cossette Juice	Diffusion Juice	Molasses	
			Found	Calcd.
Chloride	140	120	1450	720
Sulfate	130	200	2550	1200
Phosphate	400	440	230	2640
Oxalate	430	280	Nil	1680
Malate	520	320	1150	1920
Citrate	910	840	840	3440
Lactate	6	70	3300	420
Glycollate	70	4	470	64
Glyceric	Nil	Nil	Present	Nil
Hydroxybutyrate	Nil	Nil	Present	Nil

from diffusion juice to thin juice requires neutralization of the amino acids. Economically, these disadvantages may be offset somewhat by recovery of glutamic acid to be used in the manufacture of a food flavor additive.

Of the amides, asparagine is changed only slightly. Glutamine, as noted, is converted to pyrrolidone carboxylic acid. This decomposition markedly decreases the buffering capacity of beet juice (*3*, pp. 1–9) in the pH range of importance to beet technology. This is further illustrated in Figure 1, which shows the reduction in buffer capacity between diffusion, thin, and thick juice. Most of this decrease is attributed to loss of glutamine and liberation of ammonia, although some is a result of precipitation of phosphate and citrate (*3*, pp. 1–9). The importance of this decrease in second carbonation is that the carbonation to pH 8.5 to 9.2 must be carefully controlled to prevent dissolution of calcium salts. The loss of buffering capacity increases the difficulty of controlling the pH in the desired range. Moreover, if the ammonia liberated from glutamine is removed during evaporation, there are deleterious effects on the operation of the evaporators. The pH drop may be sufficient to require addition of sodium carbonate to prevent inversion of sucrose. If, however, aeration during carbonation is effective in removing ammonia, there will be an equivalent increase in calcium concentration with resultant increase in scaling and other problems arising from lime salts (*9*).

Nonamino Organic Acids and Inorganic Anions

The methods of analysis of the organic acids and inorganic anions have been described (*12*, *17*). Table III summarizes the results from the samples from the Moorhead factory. Chloride increases for reasons not specifically known. Some may have been introduced in battery supply water and some in the lime. The increase in sulfate probably arises from oxidized sulfur dioxide which is used in sulfitation. Phosphate, oxalate, and citrate decrease because of the limited solubility of their calcium salts. Malate is lower in the diffusion juice than in the cossette juice, indicating that enzymes are operating longer in the beets entering the diffuser than those immersed in the boiling alcohol. The increase in lactic acid in diffusion juice is the result of fermentation in the diffuser (*16*). The further increase in lactic acid, and the increase in glycolic, glyceric, and an unknown acid, possibly a hydroxybutyric acid, are believed to result from alkaline degradation of sugars. Usually it is considered that only invert sugar is involved. Often overlooked is the possibility that sucrose can be degraded under conditions existing in the beet factory (*15*).

Recent experiments carried out in this laboratory and in England (*3*, pp. 37–52) show that appreciable sucrose degradation can occur in the defecating, thickening, and evaporating operations. The hydroxy acids just mentioned have all been found in alkali-treated sucrose solutions.

The formation of these acids is a matter of serious concern to the sugar technologist. They increase the amount of lime or of sodium carbonate that must be added to maintain the alkalinity of the pan liquors. They may contribute to increased color. They undoubtedly increase molasses, unless the crystallizer capacity is sufficiently great to overcome the possible decreased rate of crystallization of sucrose in the presence of these impurities.

Alcohol-Insoluble Compounds

The third group of compounds which deserve consideration is the colloidal material. The results with these are not so accurate as those reported above because rapid, accurate methods of isolation of trace quantities of high-molecular-weight compounds are not well developed. The results obtained on materials from a factory in Manteca, Calif., are given in Table IV. Included are those of Eis and coworkers (*6*) on saponin which is colloidal but soluble in aqueous alcohol. It is a floc former in certain samples of beet sugar (*19*).

Boiling water extracted more pectin from the cossettes than did water at 70° to 80° C. in the diffuser. This was also true with araban and galactan. They were present in the diffusion juice by chromatographic test, but were not determined because of the small quantities present. Pectin, protein, and saponin were almost completely removed by defecation. Work is under way on the nature of beet saponins to determine why one of them tends to pass through purification and how it can be economically removed.

Inorganic Cationic Constituents

The cations are primarily potassium and sodium and go unchanged through the processing operation, although some may be added as soda ash or as impurities in water and lime rock. These ions

Table IV. Colloidal Constituents of Beet Juices

(Manteca, Calif. Mg./100 g. sugar)

Constituent	Cossette Juice	Diffusion Juice	Thick Juice
Saponin fraction[a]	...	380	(20)
Alcohol insol.	1780	430	90
AUA[b]	1200	50	15
Arabinose	250	...	..
Galactose	125	...	..
Protein[c]	200	260	2

[a] (*6*).
[b] Anhydrouronic acid.
[c] 6.25 × N.

have been thoroughly studied by beet technologists (*4*) and have not been investigated further here.

Importance of Composition Studies

One example of the practical importance of composition studies is the finding of significant quantities of lactic acid in diffusion juice. Examination proved that it was mainly artifact and indicated greater losses of sugar than had been assumed by technologists. Work already under way in the beet factories on use of formalin to prevent lactic fermentation was further stimulated. Recent reports show that such fermentation can be almost eliminated by intermittent additions of large amounts of formalin or paraformaldehyde and by judicious increase in temperature of battery supply water (*10, 11, 14*). This could lead to a saving of several hundred thousand dollars worth of sugar (including reduction in molasses formation). Even the sketchy information available indicates that further savings can be made by decreasing degradation of sucrose in limers, carbonators, thickeners, and evaporators.

The data from the composition study prove that lime is not effective in removing many impurities from beet juice. Its main recommendation is that it forms an economical filter aid during carbonation and that it removes most of the colloidal impurities, and oxalate, citrate, and phosphate. Attempts to improve purification might well be directed to other operations, particularly towards the diffuser. The greater the elimination of impurities accomplished there, the simpler will be the purification step. The processing unit financed by the Beet Sugar Development Foundation, and to be constructed at this laboratory, will enable thorough investigation of the diffuser as a purifier.

The possibilities of improving the processing qualities of beets through breeding and agronomical practice require continued study. In California, and possibly other areas as well, sugar content of beets has been decreasing while impurities unremoved by lime have been increasing. This decreases the amount of recoverable sugar and emphasizes the importance of a thorough statistical study on the correlation of agronomical factors with processing quality of beets to establish the optimum level of fertilization and irrigation.

Compositional knowledge can also aid in the evaluation of new processes. Mechanical disintegration methods, such as ultrasonics or steam explosion of beet cells, are likely to increase colloidal impurities. This, in turn, is likely to require special purification methods, such as predefecation, to obtain rapidly filtering juices (*5*).

Composition and Processing Qualities of Sugar Beets The possibility of using analytical techniques to determine the processing quality of beets has been greatly enhanced by the increase in knowledge of composition. Thus, it was found that in the 13 molasses samples analyzed in this laboratory there was 0.97 mole of sugar per equivalent of anionic material and 1.25 moles per gram atom of nitrogen. These two easily measured quantities may provide a basis for calculating yield of molasses from a beet variety. They may be supplemented by analyses for specific materials such as saponin or protein which contribute to foaming and filtration problems in the factory.

By-Products from Sugar Beets Knowledge of composition necessarily precedes development of chemical by-products. Now that the nature of compounds in beets is established, it is possible to evaluate by-product possibilities. Sugar beets offer one advantage for further utilization because the product of 12,000,000 tons of beets is collected at less than 80 sites. The molasses from about 6,000,000 tons of beets is collected in about 20 factories. Cost of disposal of wastes and the nuisances arising from them when they are ponded or dumped into streams also add to the incentive to utilize the beet further. At the present rate of production of beet sugar, 1,800,000 tons, the amount of betaine available is about 30,000 tons; glutamic acid and citric acid are about 15,000 tons each; and other amino and nonamino acids are present to the extent of at least 1000 tons each. This compares to an annual consumption of 25,000 tons of citric acid.

At present only a few thousand tons of glutamic acid are recovered for sale as a flavor adduct. The betaine and amino acids, which remain after glutamic acid removal from the waste liquors, are sold as a feed supplement. Whether or not economical methods for the isolation of other chemicals from beet wastes can be developed is a moot question. Replacement of the present lime-carbonation purification with ion exchange units might increase interest in by-product utilization. Difficulties in plugging of columns, inversion of sucrose, decreased heat economy, and cost of regenerants militate against use of resins in the beet factory. The answer to these problems may lie in future development of the electrolytic membrane technique (*7, 8*).

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