The Effect of Various Impurities on the Crystallization of Sucrose

GUY RORABAUGH AND LLOYD W. NORMAN[1]

Introduction

The physical phenomena which control the rate of crystallization of sucrose from solution are not well defined. Although much work has been done on the subjects (1)[2] sucrose-salt solutions, (2) sucrose-non-sucrose solutions, (3) and real massecuites (4) indications are that the Noyes-Whitney-Nernst equation, which assumes that diffusion of the sucrose molecules to the crystal surface is the rate controlling mechanism, is not valid. Rather it is shown, that the rate closely approximates that of a unimolecular reaction, particularly when sucrose activities are utilized rather than concentrations.

The effect of purity upon the crystallization of sucrose from beet-house sirups has been clearly shown by Nees and Hungerford (5). Seasonal and district variations are indicated by the same work and also by the later work of Hungerford (6). It is the general belief, that all impurities associated with natural beet sirups impede crystallization, although Suzuki (7) has obtained evidence (not well verified) of a beneficial action by traces of manganese sulfate.

Van Hook and Shields (2) have separated the impurities found in natural sirups into two groups: the electrolytes or ash portion and the non-electrolytes or organic non-sugar constituents. In each case, they have correlated satisfactorily their own data as well as that of other workers (8) (9) with the activity concept of crystallization behavior.

Data on the relative inhibitory effect of impurities normally found in beet sirups are rather meager. Amagassa has reported on several salts, including Na_2CO_3, K_2CO_3, NaCl, KCl, $NaC_2H_3O_2$, $KC_2H_3O_2$ and Na_2SO_4, listed in the approximate decreasing order of their effect upon crystallization (8). Other workers confirm the inhibitory power of salts, but generally do not compare their relative effects.

Of the organic non-sugars, the inhibitory power of raffinose has been given considerable attention (6, 3). Other materials on which work has been reported include invert sugar, dextrose, amino acids, and caramel (3, 10, 9). European literature contains many references to "noxious nitrogen" and "harmful nitrogen" with no definite information as to the exact role of individual nitrogenous substances as molasses formers or their effect on crystallization.

The solubility of pure sucrose in water has been determined by several workers with the data of Herzfeld (11), published in 1892, having been accepted more or less as standard, even up to the present time. However, information regarding the solubility of sucrose in solutions of the common sugar-house impurities is limited. Brown and Nees (12) have determined

---

[1] Research Laboratory Manager and Chemical Engineer, respectively, Holly Sugar Corporation, Colorado Spring, Colorado.

[2] Numbers in parentheses refer to literature cited.

the solubility in a wide variety of beet-house sirups. Jackson and Silsbee (13) have measured the solubility in invert sugar solutions. Shukow (14) determined the amount of sucrose which would dissolve in various salt solutions, and Kelly (15) more recently determined the equilibria of some similar ternary systems.

The desirability of segregating the relative effects of the various impurities upon the crystallization of sucrose from sugar-house sirups has long been recognized, but lack of analytical data and methods has prevented the sugar technologists from being able to control adequately, experimental conditions so that quantitative interpretation of results in terms of individual components (some of which could not even be identified) has been impossible. With the development of new analytical techniques, such as paper chromatography and ion exchange, Owens and his associates have been able to add considerably to the knowledge of the composition of beet-house sirups and juices (16, 17, 18, 19).

The present work was undertaken for the purpose of obtaining practical information regarding the relative effect of some of the more prevalent impurities found in beet sirups after carbonation upon the crystallization of sucrose. The identity and amount of these contaminants were furnished by Owens (20). Benefit resulting from determination of such relative inhibitory effect was visualized as twofold. In the first place, knowledge of which impurities cause the greatest difficulty in crystallization would allow the focusing of attention upon removal by existing, as well as supplementary, processing techniques. Also, and probably of even greater value, would be the opportunity to develop a beet breeding program aimed at eliminating or reducing the more troublesome compounds from the beet itself, since a great many of the impurities are impossible to remove in the factory with the processing methods used today. If beets can be selected to give a high sugar yield per acre and, in turn, be low in impurities that cause trouble in processing and crystallization, it follows that more sugar can be recovered per ton of beets processed and at a lower cost.

The work as developed can be divided into three separate phases. The first phase involved the use of actual beet-house massecuites which were recrystallized in the presence of known amounts of individual impurity. A second phase involved the preparation of synthetic sirups from pure sucrose and known added amounts of chosen impurities. In this case, crystallization tests were carried out both with the addition of increments of individual impurities and, also, with the elimination of such impurities. The third phase included solubility determinations of sucrose dissolved in solutions of individual impurities.

Procedures

The experimental work was carried out in a constant temperature air bath, a picture of which is shown in Figure 1.

The temperature was maintained constant by passing the air in the thermostat through slots in the false bottom, over a bank of ordinary light bulbs, through a circulating fan, and back into the main body of the thermostat. The temperature sensing element was an ordinary mercury

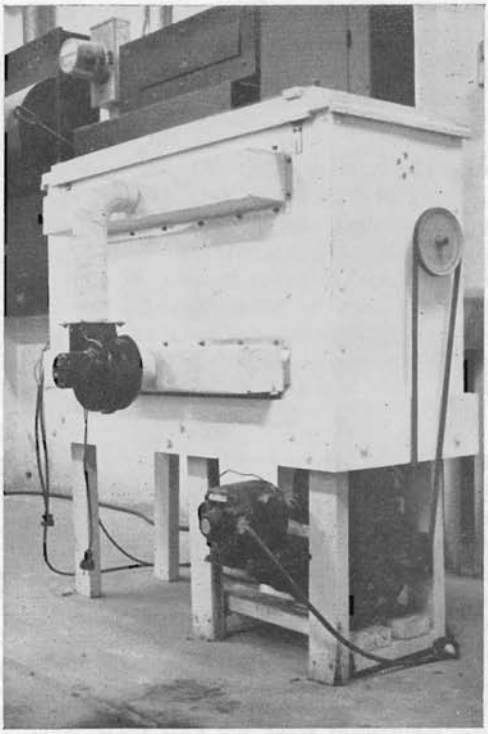

Figure 1. — Air bath for crystallization tests showing circulating fan and manifold.

thermometer and a "Thermocap" relay, which controlled the heat source. Very accurate control of temperature is possible.

The samples to be crystallized were placed in pint fruit jars held in ring adapters. This assembly was then placed in the thermostat on a pair of rubber-covered rollers which were rotated mechanically, thus turning the ring adapter and fruit jar. The jars were rotated at a speed of 1/3 R.P.M. to provide continuous gentle agitation of the sample.

In the first phase of crystallization studies reported herein, a low-raw massecuite from the Sidney, Montana, factory was employed. This massecuite had a true purity (on R.D.S. basis) of 81.76. A series of runs was conducted with this low-raw massecuite as the basic material.

A batch of the low-raw massecuite was first diluted in order to dissolve all of the crystalline sugar present. It was then evaporated under vacuum to a concentration slightly above the 1.1 supersaturation desired and finally diluted carefully with distilled water to the exact concentration as determined by the Bausch and Lomb precision refractometer. Supersaturation of 1.1 was calculated as given by McGinnis (21). Concentration of saturated beet sugar syrups at varying temperatures and purity are arbitrarily taken from Brown, et al. (22).

For each individual sample 250 grams of the base solution was weighed into a pint fruit jar and the desired impurity to be tested was added in the

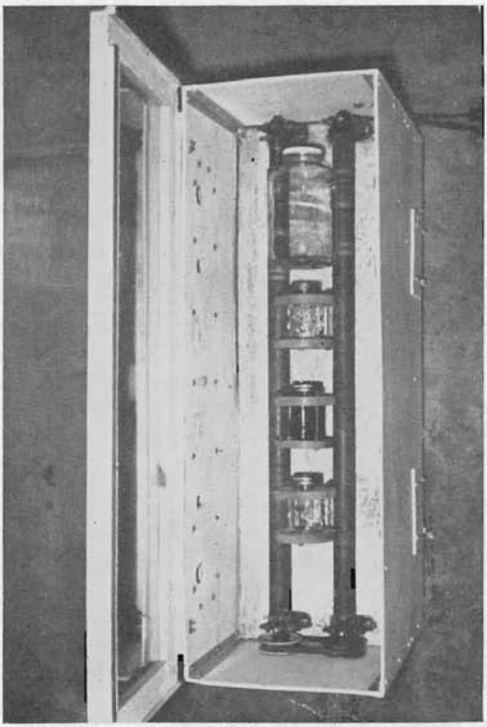

Figure 1-A.—Inside view of air bath showing rolls and adapter rings on jars.

approximate amount reported, based on its occurrence in molasses (20). After the impurities had been dissolved, the jars were fastened in the ring adapters previously described and the assembly placed in the air bath held at 120° F. The samples were held in the air bath overnight at this temperature to allow them to reach equilibrium at this temperature.

At 8:00 the following morning the samples were seeded with 75 grams of screened seed sugar (—42 + 48-mesh). Since all could not be seeded simultaneously, they were seeded individually at five-minute intervals (starting at exactly 8:00 a.m.). The air-bath temperature was arbitrarily lowered 5° F. every hour on the hour to provide a simulated crystallizer temperature pattern. The final temperature adjustment to 85° F. was made at 3:00 p.m.

At 4:00 p.m., the first seeded sample was removed and its R.D.S. determined. The remaining samples were removed and their R.D.S. determined at five-minute intervals in the order in which they were seeded. Loss in R.D.S. was taken as sugar crystallized.

In addition to the determination of crystallization after eight-hours crystallization, the samples were also allowed to remain in the air bath at room temperature for several days in order to determine total crystallization at equilibrium conditions. In these tests, all heating elements were turned off at 5:00 p.m. on the day seeded, thus allowing the temperature to drop slowly from 85° F. to room temperature (73° F.) and remain at room temperature for the rest of the test.

In the second phase of these studies, synthetic solutions of chosen impurities were employed. Two approaches to the problem were used. In the first, each individual impurity whose effect was to be studied was eliminated from one sample, with the relative increase in crystallization due to its elimination being taken as its relative inhibitory power. For the second approach, a stock solution of all chosen impurities was prepared and each individual impurity added in further quantity as it was tested, with decrease in crystallization being taken as a measure of melassigenic power. All impurities were tested in equal concentration except as noted.

Of necessity, in the series in which the impurity components were individually eliminated, each sample was prepared separately. Each impurity was present in the ratio of 1 part per 100 parts of sucrose except the leucines, which were added in the amount of 0.35 part per 100 parts of sucrose due to their limited solubility. A final sirup purity of 92.3 was employed in every case.

The impurities, sucrose, and water were accurately weighed into the pint sample jars to provide 250 grams of sirup at the concentration desired. The jars were then sealed and the solids dissolved by agitation of the jars in a hot-water bath. The samples were then cooled to about 55° C. and final minor adjustment of concentration to 1.1 supersaturation made according to R.D.S. As in the massecuite samples, the samples were allowed to remain overnight in the air bath at 120° F. Seeding temperature lowering, and final R.D.S. determination at eight hours and several days were also conducted in the same manner as before. Levels of pH were held the same by adjustment with potassium hydroxide to a pH of 9.

For the test series in which impurities were an added factor rather than an eliminated one, a stock solution of impurities was first prepared in the approximate ratio in which they have been found in beet molasses (20, 21), with the pH adjusted to 9. Samples were then prepared in pint jars from weighed amounts of stock solution, sucrose, and each individual added impurity. Dissolution of solids, concentration adjustment, and actual crystallization testing were all carried out in the same manner as before. Added impurities were all in the ratio of 1 part per 100 parts of sucrose except leucine, which was added in the ratio of 0.5 part per 100 parts sucrose. Some difficulty was encountered in obtaining complete dissolution of a few of the impurities with K_2SO_3 being the most troublesome. It was thought, however, that all impurities dissolved in the presence of sucrose in the hot-water bath. Whether or not some of the least soluble ones were precipitated out in the crystallization runs is not known.

The final phase of the present studies involved determination of the solubility of sucrose in solutions of some known impurities found in beet molasses. Solutions of the individual impurities were prepared in pint fruit jars in concentrations of 10 grams impurity plus 100 grams water, except aspartic and glutamic acids which were saturated solutions (at 30° C.). After the solutions were allowed to reach equilibrium at 30° C. an excess of -/+ 42-mesh crystalline sugar was added. The jars were then replaced in the air bath at 30° C. and allowed to remain with constant slow

agitation for six days. The jars were then removed and R.D.S. determined in order to calculate the amount of sucrose dissolved.

Results—Phase I, Natural Sirups + Added Impurities

The effect of several chosen impurities upon crystallization from a low-raw massecuite base stock was determined by the methods previously described. The impurities chosen for the tests are shown in Table I.

In eight-hour crystallization tests, all of these impurities significantly lowered the crystallization rate (to 1 percent level of statistical significance), except betaine.

A check of the precision of the method of running the crystallization tests was deemed an essential factor in the early runs in order to prove the usefulness of the method. In a series of tests involving three replications of seven treatments, it was found that the standard deviation among replications was 0.028 R.D.S.

This small deviation between replications and the fact that differences between treatments in the order of 0.10 R.D.S. were found significant to the 1 percent level indicates that the method should be very useful in detecting small changes in crystallization rate. It also points up the fact that extreme care must be used in preparation of samples for testing, as well as in the actual measurements involved.

Included in Table I is a list of the various impurities used in decreasing order of their crystallization inhibitory power. The first column shows the relationship at the approximate concentration level known to exist in certain beet sirups. The second column gives the list on the calculated basis of equal concentrations of 1 part per 100 parts of sucrose. This was calculated by the difference in R.D.S. obtained divided by the parts of impurity per 100 parts sugar used in the test. This may not be necessarily true as it assumes the effect is linear with concentration; however, it provides a relative effect of the individual impurity.

Table I.—Impurities Given in Decreasing Order of Their Effect Upon Crystallization.

Actual Concentration Basis	Equal Concentration Basis
1. Betaine	Calcium chloride
2. Glutamic acid	Serine
3. Aspartic acid	Calcium sulfate
4. Leucines	Aspartic acid
5. Sodium sulfate	Leucines
6. Alanine	Glutamic acid
7. Serine	Alanine
8. Calcium chloride	Sodium sulfate
9. Calcium sulfate	Betaine

It is immediately apparent that the difference in basis makes a great difference in the relative ranking of the melassigenic power. Although the unit effect of betaine is the lowest of any of those impurities tested, its cumulative effect, due to its rather high concentration in beet sirups, is the greatest of any. Conversely, the two calcium salts and serine are present in such small quantities that their effect is relatively small, but if they were

present in equal concentrations to the other materials their effect would top the list.

Results—Phase II, Part 1—Synthetic Sirups with Individual Impurities Eliminated

In the second phase of the present work synthetic sirups were employed exclusively. The synthetic sirups were comprised of purse sucrose, water, and chosen impurities known to exist in beet-house sirups in significant quantities. Besides the synthetic nature of the sirups, the tests in this phase of the work also differed from the first in another important respect. Whereas impurity concentrations approximating those found naturally in beet-house sirups were employed with the natural sirups, equal weight concentrations were used with the synthetic sirups unless solubility limitations prevented. By using equal concentrations the relative melassigenic effects of the individual impurities could be compared directly.

Since the impurities to be studied in this series of tests were eliminated from the individual samples, their inhibitory effect was also eliminated. Thus, in the results of these tests the crystallization was greater for those samples which have the greater inhibitory power. In Table 2 are shown the results of this series of runs with data taken at 8-hours, 24-hours and 4-days crystallization time.

Table 2.—Synthetic Sirups With Individual Impurities Eliminated.

	8-hours Crystallization		24-hours Crystallization		4-days Crystallization	
Impurity Eliminated	R.D.S.	Percent Crystallization	R.D.S.	Percent Crystallization	R.D.S.	Percent Crystallization
Malic acid	71.66	74.00	70.62	85.71	70.50	88.09
Lactic acid	71.65	75.90	70.62	85.71	70.49	88.27
K_2SO_4	—	—	70.46	89.15	70.42	89.91
Betaine	71.58	77.14	70.49	88.19	70.37	90.56
Leucines	—	—	70.37	90.75	70.32	91.70
Glutamic acid	71.41	80.20	70.40	89.92	70.27	92.48
Aspartic acid	71.44	79.01	70.37	90.56	70.26	92.71
P.C.A.	71.41	80.48	70.37	90.49	70.25	92.84
KCl	- -	—	70.28	92.50	70.72	93.63
Alanine	71.36	81.57	70.32	91.59	70.14	95.06

NOTE: All impurities present in concentration of 1 part per 100 parts of sucrose except leucines which, due to low solubility were added in concentration of 0.35 part per 100 parts sucrose.

A plot of crystallization time versus percent crystallization realized is given in Figure 2 for the fastest and slowest crystallizing sirups, as well as two intermediate ones. The curves show that after about 2½ days' time little additional crystallization takes place and, therefore, any crystallization time greater than this could be considered essentially at equilibrium conditions. The following list shows the impurities in order of the decreasing effect upon the crystallization.

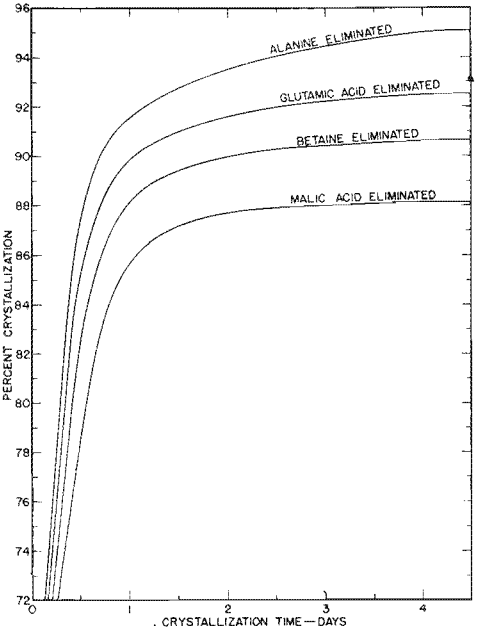

Figure 2.—Percent crystallization versus time.

Table 3.—Some Beet-House Impurities in Order of Their Decreasing Effect Upon Crystallization of Sucrose From Synthetic Sirups.

1. Leucines[1]	6. Glutamic acid
2. Alanine	7. Betaine
3. Potassium chloride	8. Potassium sulfate
4. P.C.A.	9. Lactic acid
5. Aspartic acid	10. Malic acid

[1] Leucines corrected to 1 part per 100 sucrose. Ranked between glutamic acid and betaine on .35/100 as tested.

A comparison of this table with the results obtained for both eight-hours crystallization and one-day crystallization will show only minor changes in the order between impurities which have been very close to the same effect. Similarity of the results to those obtained with natural sirups, as given in Table 1, will also be noted.

In order to assign a specific value in terms of the amount of sucrose lost (held in solution) per unit weight of impurity, we assumed that malic acid has little or no effect upon the crystallization; actually, it had the least effect. Thus, if the difference between the effect of malic acid and each of the other impurities is determined, an arbitrary measure of the amount of sucrose lost will be obtained. In effect it could then be said that, if malic acid could be exchanged for the impurity involved, an increased recovery of sucrose could be realized. Under the condition of these tests and the assumption above, the following increase in sugar recovery could be realized in pounds sucrose per pound of impurity per 100 pounds original sucrose in solution before crystallization.

Table 4.—Increased Sucrose Recovery Obtained by Exchange of Malic Acid For Other Impurities.

Impurity	Pounds Additional Sucrose
Lactic acid	0.07
Potassium sulfate	0.60
Betaine	0.62
Glutamic acid	1.28
P.C.A.	1.32
Aspartic acid	1.42
Alanine	2.55
Leucines[1]	3.43

[1] corrected to 1 part/100 parts sucrose.

A comparison of this nature shows up the practical significance of the difference in effect of the various impurities. For instance, those impurities which have the greatest effect per unit of weight are severalfold more troublesome than those on the lower end of the group.

Phase II, Part 2—Synthetic Sirups with Added Impurities

To provide a better basis of calculations of the amount of sucrose held in solution by a given weight of impurity and to make further comparison of the relative effect of various impurities upon the crystallization of sucrose, additional tests were conducted which consisted of crystallization runs in which known amounts of individual impurities were added to a synthetic stock sirup of known composition. Not only could the relative effect of each impurity be determined, as in the tests described earlier, but also the specific effect of each could be calculated in comparison to crystallization from the basic stock sirup.

In these tests, since the impurities were added to a basic sirup, the effect will be a lowering of the crystallization. The relative crystallization for 4-day and 6-day tests is presented in Table 5.

Table 5.—Relative Crystallization Obtained With the Addition of Selected Impurities to a Synthetic Base Sirup.

Impurity Added	4-days Crystallization		6-days Crystallization	
	R.D.S.	Percent Cryst.	R.D.S.	Percent Cryst.
K_2CO_3	71.07	60.82	70.98	62.28
KCl	70.88	63.88	70.77	65.64
Leucine	70.68	67.08	—	—
Glutamic acid	70.75	65.96	70.67	67.24
Alanine	70.74	66.12	70.64	67.69
Aspartic acid	70.73	66.28	—	—
P.C.A.	70.67	67.21	70.57	68.81
Lactic acid	70.64	67.69	—	—
Malic acid	70.62	68.01	70.52	69.59
Betaine	70.58	68.65	70.49	70.04
K_2SO_4	70.54	69.27	70.46	70.52
Check	70.54	69.27	70.48	70.20

NOTE: All added impurities present in the amount of 1 part per 100 parts sucrose except leucine, which was added in the amount of 0.5 part per 100 parts sucrose.

As noted in the previous series, the crystallization had nearly reached equilibrium conditions after four days. Although there was a measurable drop in R.D.S. between four and six days, the amount was small and virtually constant for all samples, being from 0.08 to 0.11 R.D.S. units. No differences at all could be measured, for a few chosen samples, between the six-day readings and readings after 10-days crystallization.

Some changes in ranking will be noted from Table 5 in comparison with previous results. Potassium carbonate, which was not included in other tests, proved to be the worst offender of all. Alanine dropped a couple of notches, and P.C.A. and glutamic acid more or less "swapped" positions. Lactic and malic acids, which were previously the least inhibitive, climbed above betaine and potassium sulfate, although all of there were relatively low. Nevertheless, the same general pattern persists in that the previously high ranking impurities still ranked high and the low ones still low.

The "check" sample included in this series of tests provides a good basis upon which to calculate the absolute amount of sugar lost (held in solution) by a given quantity of each impurity, since the "check" sample consisted of the basic sirup only without added impurity corrected to the same R.D.S. and purity as the other solutions. The difference between the absolute quantity of sugar crystallized from each sample and that crystallized from the "check" sample will give the quantity of sugar lost per unit of impurity added per 100 units of sucrose in the original sirup at the purity employed (86.0 in original sirup). It should be recognized that, since the effect upon crystallization is not directly proportional to concentration, other concentrations at other purities would not necessarily give the same values. Yet, as already pointed out, such figures will be more significant in estimation of actual dollars and cents loss and will show clearly the area in which elimination of specific impurities, regardless of method of elimination, will be most profitable.

In Table 6 are presented the relative quantities of sugar lost in terms of pounds per pound of impurity per 100 pounds sucrose originally present.

Table 6.—Pounds of Sucrose Lost Per Pound of Individual Impurity Per 100 Pounds of Sucrose Originally Present.

Impurity	Pounds Sucrose Lost
Potassium carbonate	3.70
Potassium chloride	2.36
Leucine[1]	1.94
Glutamic acid	1.45
Alanine	1.38
Aspartic acid	1.31
P.C.A.	0.89
Lactic acid	0.69
Malic acid	0.55
Betaine	0.27
Potassium sulfate	—

[1] Corrected to concentration of 1 part per 100 parts sucrose.

Again, it will be noted that the impurities having the greatest effect upon crystallization hold several times as much sucrose in solution as those which have the least effect. If we now combine the additional factor of concentration with the sucrose holding power, as given above, while keeping in mind the fact that the effect need not be directly proportional to concentration, a good indication is obtained of the total melassigenic power of some of the major impurity constituents found in beet-house sirups.

In Table 7, is given the average composition for molasses as furnished by Owens (20), and the total sugar which would be held in solution by such quantity of impurity based upon the data given in Table 6.

Table 7.—Total Sugar Lost in Molasses by Crystallization Inhibiting Effect of Some Chosen Impurities.

Impurity	Average Occurrence in Molasses (grams/100 grams Sucrose)	Total Sugar Held by Impurity (pounds/100 pounds Sucrose)
Potassium carbonate[1]	8.00	29.60
Potassium chloride[2]	8.00	18.88
Leucines	0.35	0.68
Glutamic acid	1.25	1.81
Alanine	0.85	1.17
Aspartic acid	0.90	1.18
P.C.A.	5.50	4.90
Lactic acid	2.80	1.93
Malic acid	1.00	0.55
Betaine	9.00	2.43
Potassium sulfate[2]	3.70	—
TOTAL:	41.35	63.13

$$\text{Purity} = \frac{63.13}{104.48} \times 100 = 60.42$$

[1] Not reported by Owens. Taken here as equal to chloride content. Carbonate reported elsewhere (21) as over twice the chloride.

[2] Chloride and sulfate content as the potassium salt.

Table 7 provides food for thought along several different lines. In the first place, it will be seen that over 75 percent of the total sugar held in molasses is there as a result of two of the ash components, potassium carbonate and potassium chloride. Not only are these compounds the two top inhibitors of sucrose crystallization, but they are also high on the list of average occurrence. Thus, their combined effect becomes a large fraction of the total effect of all impurities.

We have found very little in the literature on the concentration of carbonate in molasses or other beet-house sirups. In McGinnis' text on "Sugar Beet Technology" (p. 139) a typical analysis for California molasses shows carbonate content over twice that of chloride. We have arbitrarily taken the carbonate content as equal to the chloride. Therefore, if the carbonate content were doubled, it alone would account for over 60 percent of the sucrose loss. Regardless, however, it appears that any measures which can be taken to lower the carbonate and chloride content of beet sirups

would be of great benefit. Following the carbonate and chloride salts, the amino acids and betaine are next most troublesome. Next in line come the non-nitrogenous organic acids and, last, with little or no apparent harmful effect, will come the sulfate salts.

Of the nitrogen compounds, P.C.A. plus glutamic acid have the greatest total effect upon crystallization primarily because of their relatively high concentration. Their combined effect is over 10 percent of the total and, thus, comprises a significant portion of the sugar loss.

It is fortunate, indeed, that betaine has a relatively small effect upon crystallization. Betaine provides nearly 22 percent of the total impurities, as given in Table 7, yet less than 4 percent of the sucrose loss is attributed to the compound. On the other hand, the leucines and alanine are relatively high in the ranking of inhibitory power, but their limited concentration makes them a small factor in over-all molasses forming tendency.

Malic and lactic acids are present in molasses in significant quantities, but they do not contribute greatly to sucrose loss since they are not strongly melassigenic.

Potassium sulfate, at least in these tests, is in a class by itself. Little effect upon crystallization was indicated.

Phase III—Solubility of Sucrose in Some Solutions of Selected Impurities.

In this final phase of the present studies, a brief series of tests were conducted in which the solubility of sucrose was determined in some solutions of several of the impurities studied in the crystallization tests. These tests were conducted at a constant temperature of 30° C. in the same equipment used in the crystallization studies. Table 8 gives the results of the solubility tests.

Table 8.—Solubility of Sucrose in Solutions of Some Selected Impurities.

Impurity	Final R.D.S.	Solubility grams Sucrose/100 grams H_2O	R.D.S. of Impurity Solution
P.C.A.	74.12	276.4	8.96
Betaine	68.14	203.9	7.83
Malic acid	73.45	266.6	7.92
Alanine	69.08	213.4	10.72
Glutamic acid[1]	68.58	208.3	1.34
Aspartic acid[1]	68.78	210.3	0.80
Potassium carbonate	70.88	233.4	16.28
Potassium chloride	69.58	218.7	8.33
Potassium sulfate	68.79	210.4	7.41
Sodium carbonate	71.04	253.3	13.10
Sodium chloride	69.67	219.7	10.65
Sodium sulfate	68.49	207.4	9.10
Check	68.52	217.7	—

[1] Saturated solution (at 30° C.) employed for Aspartic and Glutamic acids.

The results of the solubility tests seem to point out several things. In the first place, the results should be fairly accurate, since the solubility of sucrose in water (the "check" sample) is in good agreement with the value

of Herzfeld (11). The data for solubility in salt solutions checks the crystallization results in that the order of effect of carbonate-chloride-sulfate corresponds to the same order of effect found in the crystallization tests. These tests also provide a comparison of potassium with sodium and indicate that sodium should be more harmful than potassium. This relationship has been given previously in the literature (8).

Betaine is shown to hold a low amount of sucrose in solution, also in agreement with the crystallization results reported herein. The effect of the amino acids does not check well with the crystallization results, and an even greater discrepancy is noted for malic acid, which allowed the second greatest solubility of sucrose.

A recent paper by Wiklund (23) suggests the presence of molecular compounds between sucrose and salts which, if his hypothesis is valid, would help explain some of the differences in solubility not following the results obtained by crystallization.

The last column in Table 8, giving the R.D.S. of the impurity solution before the addition of sugar, is included to show the R.D.S. variations of the various materials. R.D.S. for the impurity solutions (except glutamic and aspartic acids) should have been 9.09, since 10 grams were dissolved in 100 grams H_2O. If we take the greatest variation from this 9.09 figure we find sodium carbonate to be 4.01 higher and malic acid to be 1.76 lower. At a total solids of about 220 grams/100 grams H_2O this variation would amount to 0.9 to 1.8 percent deviation.

Discussion of Results

In general, the order in which some of the common beet-sirup impurities affect crystallization was found to be as follows:

1. Carbonate and chloride salts
2. Amino acids
3. Betaine and non-nitrogenous organic acids
4. Sulfate salts

Some variation in position among individuals in these groups was encountered, but the pattern of groupings, as shown, was rather consistent throughout these tests.

It is unfortunate, indeed, that chlorides and carbonates are so strongly melassigenic, since they are present in relatively large concentrations in the beet sirups and, therefore, account for a large fraction of the total sugar lost in molasses. Yet, on the other hand, it is fortunate that betaine and the sulfate salts, also present in rather large quantities, are at the bottom of the list.

From the data which we have gathered, it would appear that the most fertile ground for improvement of the crystallization characteristics lies in the elimination of carbonate and chloride salts with lowering of P.C.A. and glutamic acid the second most likely point of attack. The former pair, which appear to account for over ¾ of the total melassigenic power, should warrant the most concentrated efforts. The latter two also rate some attention, since they contribute over 10 percent to the total.

The case against P.C.A. and glutamic acid is a two-edged one, since not only are they major contributors to sugar loss in molasses, but also decomposition of glutamine, the amide from which they originate, causes processing difficulties through lowering of buffering capacity of juice and lowering of alkalinity. At the present time no method of elimination of glutamine by processing techniques is usable in the sugar factory, thus its elimination is also in the hands of the beet breeder.

Since glutamine in Steffen waste (in the form of P.C.A. and glutamic acid) has some value as a raw material for the production of monosodium glutamate, its presence in beet juices is not a total loss. It is problematic whether lowering the amount present would increase ease of processing to a sufficient extent to offset its value in Steffen waste. On the other hand, it would seem wise to think twice before purposely increasing the glutamine content of beets merely to increase the amount recoverable from Steffen waste.

Our work has indicated that, aside from carbonate and chloride salts and the decomposition products of glutamine, the remainder of the impurities examined present in molasses account for less than 15 percent of the sugar loss. It would seem logical, then, to concentrate first on elimination of the aforementioned compounds and disregard, for the present at least, the rest of the impurities.

References

(1) VAN HOOK, A. 1944. Kinetics of sucrose crystallization pure sucrose solutions. Ind. Eng. Chem. 36:1042-47.

(2) VAN HOOK, A., SHIELDS, D. 1944. Sucrose—salt solutions. Ind. Eng. Chem. 36:1048-51.

(3) VAN HOOK, A. 1946. Kinetics of sucrose crystallization—sucrose—non-sucrose solutions. Ind. Eng. Chem. 38:50-53.

(4) VAN HOOK, A. 1948. Kinetics of sucrose crystallization—real massecuites. Ind. Eng. Chem. 40:85-89.

(5) NEES, A. R. and HUNGERFORD, E. H. 1936. Low purity beet house sirups—crystallization rates of sucrose. Ind. Eng. Chem. 28:893-97.

(6) HUNGERFORD, E. H. 1942. Seasonal and district variations in the rate of crystallization of sucrose from beet-house sirups. Proc. Am. Soc. Sugar Beet Tech. 499-514.

(7) SUZUKI, K. 1949. Manganese sulfate in sugar boiling. Sugar 48: No. 3.

(8) AMAGASSA and NISHIZAWA. 1936. Series of papers on crystallization of sugar. J. Chem. Soc. Ind., Japan. 39: Suppl. Binding 263.

(9) KUCHARENKO, I. A. 1928. Sucrose crystallization. Planter Sugar Mfg. 75.

(10) AFFERMI, E. 1934. Sucrose and raffinose in molasses. Ind. Saccar. Ital. 27:319.

(11) HERZFELD, A. 1892. Z. Ver. Deut. Zuckerind. 42:232.

(12) BROWN, R. J. and NEES, A. R. 1933. Solubility of sucrose in beet house sirups. Ind. Eng. Chem. 25:555-58.

(13) BATES, F. J., ET AL. 1942. Polarimetry, Saccharimetry and the sugars. Nat'l. Bur. of Stds., Circ. C-440:364 U. S. Govt. Printing Office.

(14) SCHUKOW, I. 1900. Z. Ver. Deut. Zuckering. 50:313.

(15) KELLY, F. H. C. 1954. Phase equilibria in sugar solutions. I. ternary systems of water—sucrose—inorganic salts. J. Appl. Chem. 4:401-404.

(16) STARK, J. B., GOODBAN, A. E. and OWENS, H. S. 1950. Organic acids in sugar beet diffusion juices. Proc. Am. Soc. Sugar Beet Tech. 578-83.

(17) OWENS, H. S., STARK, J. B., GOODBAN, A. E. and WALKER, H. G. JR. 1955. Application of compositional knowledge to beet sugar technology. J. Agr. Food Chem. 3:350-353.

(18) GOODBAN, A. E., STARK, J. B. and OWENS, H. S. 1953. Amino acids—content of sugar beet processing juices. J. Agr. Food Chem. 1:261.

(19) OWENS, H. S., GOODBAN, A. E. and STARK, J. B. 1953. Fractionation of organic acids in sugar beets by ion exchange resins. Anal. Chem. 25:1507-11.

(20) OWENS, H. S. Personal communication.

(21) MCGINNIS, R. A. 1951. Beet sugar technology. Reinhold Pub. Corp., New York, N. Y.

(22) BROWN, R. J., SHARP, J. E. and DAHLBERG, H. W. 1928. Determination of solubility of sucrose in beet-house sirups. Ind. Eng. Chem. 20:1230.

(23) WIKLUND, O. 1955. Molecular compounds between sucrose and salts. Zucker. 8:266-277.