The Relation of Beet Molasses Composition to True Purity
Part II. Statistical Evaluation

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Many studies have been made relating nonsugar composition to beet molasses purity. Most attention has probably been given to the proposal made by Dedek (2)[2] relating the equivalents of sucrose in beet molasses to the equivalents of sodium plus potassium. This ratio appears to be close to one for most beet molasses. Approximately the same ratio was confirmed by Wiklund (12) and extended by Carolan (1) to include moles of calcium. Wiklund also found that the ratio of moles of sucrose to moles of nitrogen was approximately one.

All these means of predicting the purity of molasses leave much to be desired because they imply that no difference exists in the melassigenic effect of various components. Pieck and Rens (6) attempt to overcome this difficulty by proposing that cations equivalent to certain antimelassigenic anions be subtracted from the sum of potassium and sodium. Their selection of sodium chloride as an example was particularly unfortunate since potassium and sodium chlorides seem to be among the most melassigenic compounds.

While the terms melassigenic and antimelassigenic are widely used, it must be understood that in reality all soluble nonsugars are melassigenic in the sense that they prevent complete recovery of sugar. For a given amount of sugar and water the addition of a particular nonsugar may increase the sugar recovery by decreasing sugar solubility, but in the absence of the impurity, further water may be evaporated and essentially all the sugar recovered. In this discussion the term melassigenic will be used for those substances which increase molasses purity with increasing concentration, and antimelassigenic will designate those substances which decrease molasses purity with increasing concentration. Some nonsugars increase the solubility of sucrose, others decrease it, while some may not affect it. While some substances may decrease sugar solubility, they may be deleterious

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[2] Numbrs in parentheses refer to literature cited.

because of difficulty in separating crystalline sugar from the nonsugar. Even though some nonsugars decrease the solubility of sugar, molasses would still be formed. It will be shown later in this paper that removal of some antimelassigenic compounds without removal of melassigenic ones could result in molasses of sufficiently higher purity to give a greater loss of sugar. A further difficulty in referring to specific compounds as melassigenic or antimelassigenic is that their effect on sugar solubility may vary depending on their concentration in the solution. At some concentrations, generally low, they may decrease sugar solubility while at other concentrations sugar solubility increases (5).

The analytical data presented in Part I of this study (10) were subjected to correlation analysis to determine their relationship to each other and to molasses purity. Data from the Carlton, California, sample shown in Part I (10) were excluded from this statistical study since they appeared atypical in some respects; the high reducing sugars, for example, would exert an extreme effect on some purity-composition relationships.

After data collection the important question must be answered as to the best method of determining the effect of various nonsugars on purity. Nonsugar concentrations may be expressed on the wet basis (g/100 g molasses as received), dry basis (g/100 g molasses solids), or on the impurities basis (g impurity/100 g total impurities). Table 1 shows the correlations of each variable studied against purity when the variables are expressed on each of the three bases. It is readily apparent that each method yields different results. Some variables, such as milliequivalents of anions, showing no significant correlation on the wet or dry basis have a significant correlation on the impurities basis.

The actual melassigenic properties of an impurity do not depend on the method of calculation so that the problem arises of choosing the correct procedure for evaluating the data. Useful relationships are calculated on the impurities basis, the quantity of the variable per unit of nonsugars against purity. Correlations of purity against specific impurities are invalid if calculated on the wet or dry basis because they contain a built-in spurious negative correlation. The following example will demonstrate this conclusion.

Using variable 7, milliequivalents of anions on the solids basis with average purity of 62.9059, impurities of 37.0941 and meq anions of 181.941, we can calculate the values of meq anions, (postulating no change in the ratio of meq anions to other impurities) as sugar is added or subtracted (increasing or decreas-

ing the purity). When the impurity basis is used for calculation there is no change in the value of the specific impurity as sugar is added or subtracted from a sample. However, if we add sugar to a molasses of average composition and purity to give 64 purity the meq of anions on the solids basis is 176.575 or remove sugar to give 61 purity the value for meq of anions is 191.289. The slope for this regression line is:

$$m = \frac{64 - 61}{176.575 - 191.289} = -0.20389$$

The constant for the line is calculated as follows:

$$62.9059 = (-0.20389)(181.941) + C$$

$C = 100.002$ and the regression equation becomes

$$\text{Purity} = (-0.20389)(\text{meq anions}) + 100.002$$

It is worthwhile to calculate the change due to the spurious relationship and that due to melassigenic activity. The spurious change is calculated as the difference between meq of anions at purities 64 and 61. This is

176.575 — 191.289 or —14.714

The actual change in meq anions determined from the calculated regression line on the solids basis: Purity $= (0.02370)$ (meq anions) $+ 58.5939$ or 228.105 at 64 purity and 101.523 at 61 purity. The difference is 126.582. This difference less the spurious change 126.582 — (—14.714) or 141.296 is the change in meq anions that would be expected if there were no spurious relationship. The spurious relationship for this variable is 10.4% of the total expected change. Note that the change in meq anion values or other variables are altered more at the extreme purity values than near the average purity.

A correlation of 0.64 is obtained by correcting meq anions on the solids basis for each factory sample for variation from the average value caused by the spurious relationship and determining the correlation between purity and the corrected value. This agrees very closely with the value of 0.65 obtained when the correlation is calculated on the impurities basis. Figure 1 shows the regression lines and equations for the experimental data, built in, and corrected regression lines for meq anions against purity. In a similar manner the built-in regression can be shown for data calculated on the wet basis.

Straight House Molasses

The following variables listed in Table 1 (impurities basis) show positive correlations with purity at the 5% or lower significance level: percent ash, meq sodium plus potassium, meq anions, meq potassium plus sodium less calcium and percent

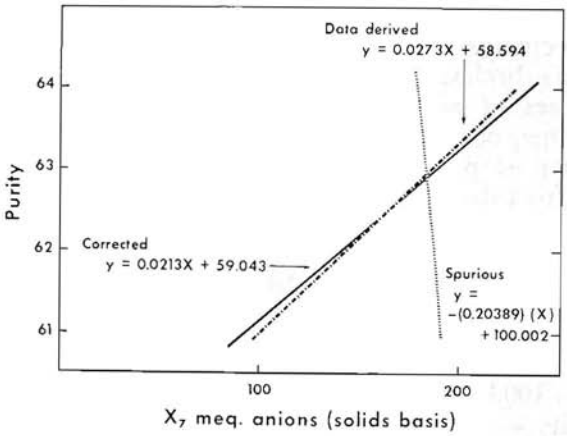

Figure 1.—Correlation of molasses purity and meq anions.

chloride. A further related variable considered here is the average equivalent weight of anions (11) which has a significant negative correlation with purity. These variables are also all highly cor-

Table 1.—Correlations of beet molasses purity and composition variable (wet, dry and impurities bases).

Variable no.	Variable identity and units	Straight house molasses[1]			Steffen molasses[2]		
		Wet	Dry	Impurities	Wet	Dry	Impurities
1	Reducing sugars, %	—.46	—.42	—.33	.75	.74	.76
2	Raffinose, %	.23	.28	.39	—.47	—.46	—.37
3	Ash, %	.08	.18	.57	—.83	—.81	—.57
4	Alkalinity of ash meq[3]	—.35	—.36	.21	—.61	—.61	—.20
5	Na + K, meq	.16	.27	.59	—.68	—.57	—.17
6	Na + K less Ca, meq	.18	.27	.54	—.53	—.45	—.15
7	Anions, meq	.05	.18	.65	—.79	—.69	—.14
8	Chloride, %	.62	.65	.71	—.13	—.09	—.01
9	Nitrate, %	.08	.13	.31	—.05	—.03	—.10
10	Anions less (Cl + NO_3), meq	—.65	—.71	—.30	—.60	—.61	—.19
11	Avg equivalent wt of anions	—.64	—.64	—.64	.26	.26	.26
12	Total wt of acids, %	—.68	—.71	—.03	—.43	—.41	.19
13	Amino N, %	—.69	—.67	—.48	.10	.11	.37
14	Total N, %	—.78	—.77	—.57	.25	.32	.57
15	Basic N, %	—.77	—.74	—.50	.09	.15	.44
16	Basic N less amino N, %	—.73	—.70	—.42	.06	.10	.36
17	Acidic N, %	—.68	—.67	—.50	.51	.56	.68
18	Acidic N less nitrate N, %	—.69	—.68	—.59	.58	.63	.72
19	Betaine, %	—.65	—.66	—.41	—.32	—.29	.01
20	Basic N less (betaine N + amino N), %	—.50	—.45	—.21	.30	.34	.43
21	Basic fraction solids, %	—.76	—.75	—.51	—.01	.07	.34
22	pH	.30	.30	.30	—.83	—.83	—.83

[1] 17 factories

[2] 13 factories

[3] milliequivalents

Table 2.—Correlation of straight house molasses variables - impurities basis[1]

Variable no.	Variable identity	Variable number																			
		3	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	Purity
1	Reducing sugars	—.73	—.70	—.76	—.51		—.50		.48		.51	.52	.58	.52				.65		—.73	
2	Raffinose						.48	—.54		—.59	—.51	—.64	—.57	—.51		—.58			—.52		
3	Ash		.97	.95	.91	.70	.50		—.87		—.61	—.70	—.64	—.55	—.55	—.73		—.60	—.60	.79	—.57
4	Alkalinity of ash																				
5	Na + K			.99	.94	.80	.57		—.87		—.54	—.66	—.65	—.60		—.68		—.49	—.64	.79	.59
6	Na + K less Ca				.87	.73	.61		—.81		—.52	—.66	—.67	—.64		—.69		—.56	—.64	.83	.54
7	Anions					.88			—.90		—.49	—.60	—.52			—.60			—.56	.57	.65
8	Chloride								—.85			—.55	—.48			—.48	—.57		—.51		.71
9	Nitrate																			.66	
10	Anions less ($Cl + NO_3$)																.52				
11	Avg equivalent wt of anions										.52	.71	.56	.48	.63	.72			.54	.64	—.64
12	Total wt of acids																				
13	Amino N											.82	.79	.52	.55	.62		.55	.65	—.53	—.48
14	Total N												.90	.78	.77	.80	.56	.64	.83	—.56	—.57
15	Basic N													.94	.52	.63	.69	.74	.91	—.64	—.50
16	Basic N less amino N															.51	.80	.71	.89	—.59	
17	Acidic N															.89		.49			—.50
18	Acidic N less nitrate N																	.55	.51	—.63	—.59
19	Betaine																		.77		
20	Basic N less (betaine N + amino N)																		.57	—.60	
21	Basic fraction solids																			.53	—.51
22	pH																				

Correlation significance
1% 0.605 2% 0.557 5% 0.482

[1] All correlation coefficients were calculated but only the statistically significant ones are shown.

related with chloride (Table 2). Is the correlation of these variables with purity significant if the extent of their dependence on chloride were removed? Meq of anions less meq of chloride have a nonsignificant correlation [—0.16] with purity. The significant correlation for meq of anions (variable 7) thus appears to be due to its chloride component. The correlation of meq of sodium plus potassium with purity is 0.59. Assume chloride to be present in molasses as sodium and potassium chlorides and subtract the meq of chloride in each sample from the total meq of sodium plus potassium. The correlation of the remaining sodium plus potassium with purity is then a non-significant 0.17. This demonstrates that the correlation of meq of sodium plus potassium with purity is mainly dependent on changes in these cations to compensate for variability in chloride. The same observation is true of percent ash since the correlation between ash (variable 3) and meq sodium plus potassium (Table 2) is 0.97. The average equivalent weight of anions has a negative correlation with purity of —0.64. This variable also has a high negative correlation of —0.85 with chloride showing that over 70% of the variability in average equivalent weight of anions is due to variability in chloride. Without the chloride component average equivalent weight of anions does not show a significant correlation with purity ($r = -.16$). The factors, meq anions, percent ash, sodium plus potassium, meq sodium plus potassium less calcium and average equivalent weight of anions are only correlated with purity because of their chloride component or high correlation with the strongly melassigenic component chloride.

The magnitude of the chloride effect is shown by the following calculation. Using the regression equation for purity (Y) and chloride (X) on the impurities basis: $Y = 0.75\,(X) + 60.344$ we can calculate the effect of one pound of chloride on carrying sugar into molasses. Taking the average molasses of 62.906 purity, 37.094 impurity and chloride of 3.415% we can see from the regression equation that removal of all chloride (chloride of 0.00%) would yield a molasses of 60.344 purity and impurity of 39.656. One hundred pounds of average impurities at 62.906 purity would carry along 169.585 pounds of sugar or about 1.7 pounds of sugar per pound of impurities. Removal of the 3.415 pounds of chloride would leave 96.585 pounds of impurities with molasses at 60.344 purity. This amount of impurities at 60.344 purity would carry 146.972 pounds of sugar into molasses. The removal of the chloride shows 169.585 — 146.972 or 22.613 pounds less sugar carried into molasses or 6.62 pounds of sugar per pound of chloride. This value is slightly higher than that reported by other investigators who obtained

their values by adding the specific impurity and sugar to a factory molasses. P. M. Silin (9) reporting the results of Z. A. Silina shows a value of 2.48 pounds of sugar removed for one pound of KCl. This is equivalent to 5.5 pounds of sugar for one pound of chloride. Rorabaugh and Norman (7) find 5 pounds of sugar lost per pound of chloride as KCl.

Factories using water or processing beets with a high chloride content that yields molasses containing six pounds of chloride per hundred pounds of impurities appear to be losing nearly 40 pounds of sugar more than if chloride were absent. Removal of this chloride should produce a gain of 40 pounds of sugar.

Chloride determinations can be used to predict molasses purity and amount of molasses produced. It will be shown in another paper that molasses purities may be predicted from the chloride content of thin or thick juices. Another way of showing the importance of this effect of chloride on molasses purity is to examine the amount of sugar carried into molasses per pound of impurity at 60 and 65 purity. Nearly 24% more sugar is carried into molasses at 65 purity than at 60 purity. The data from the present study show that 50% of the variability in molasses purity over the purity range studied is due to variability in chloride content.

The following variables have a significant (5% level or lower) negative correlation with purity: average equivalent weight of anions, amino nitrogen, total nitrogen, basic nitrogen, acidic nitrogen, acidic nitrogen less nitrate, nitrogen and basic solids. As stated previously the negative correlation of average equivalent weight of anions with purity is due to changes in chloride content. The remainder of the variables showing negative correlations are also complex mixtures but have one type of component in common: nitrogen containing compounds. Such compounds generally decrease the solubility of sugar and yield a lower purity molasses (7,8).

Since total nitrogen is negatively correlated with purity it might be thought that a multiple regression equation involving total nitrogen and chloride would give a much better estimate of purity than chloride alone. Unfortunately this is not the case. The multiple regression equation for these two variables is:

$$\text{Purity} = 0.60669\,(\%\text{Cl}) - 0.61093\,(\%\text{N}) + 64.6206$$

The correlation coefficient is 0.743 and the standard error of estimate is 0.716. This standard error of estimate is little better than the 0.723 obtained using only percent chloride for purity estimates.

The negative correlation of nitrogen content and purity is shown not only by this work but also by some Belgian results.

Several factory campaign averages in Belgium for the years 1957-1961 are plotted in Figure 2, (3,4). The regression equation and slopes for the Belgian results are compared with the data presented here. Figure 2 shows that the slopes of the two equations are very similar, and that nitrogen content is related to purity in both cases.

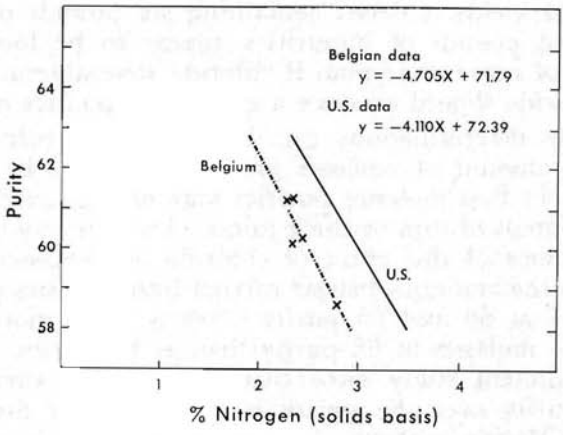

Figure 2.—Molasses purity and total nitrogen—comparison of Belgian and U. S. Data.

It is more difficult to determine the antimelassigenic effect of the nitrogen containing fractions since all are comprised of more than one compound. The nearest we can come to estimating this effect is to use variable 18 (acidic nitrogen less nitrate nitrogen). After removal of nitrate nitrogen most of the remaining acidic nitrogen is pyrrolidone carboxylic acid (PCA). Assuming that it is all PCA, we can develop the following relationship using the regression equation for variable 18: $Y = -2.8954\,(X) + 66.694$. Converting from acidic nitrogen to PCA the equation becomes: $Y = -0.314\,(X) + 66.694$. The values for the average molasses are $Y = 62.906$, $X = 12.06$ with impurities of 37.094. The value for X is estimated on the basis that all the acidic nitrogen less nitrate nitrogen is present as PCA. Actually this is a high value since approximately only 85% of this nitrogen is present as PCA. If we remove one pound of PCA from 100 pounds of molasses impurities, we have remaining 99 pounds of impurities with a PCA content of 11.17%. The purity of this molasses would be: $Y = [-0.314]\,[11.17] + 66.694$ or $Y = 63.187$. The 99 pounds of impurities at 63.187 purity would carry 169.927 pounds of sugar into molasses. The original 100 pounds of impurities carried 169.585 pounds of sugar into mo-

lasses. The removal of one pound of PCA shows 0.34 pound more sugar going to molasses even though there is one pound less of impurities. Unfortunately, no reliable data are available on the solubility of sucrose in the presence of PCA salts to confirm or deny the antimelassigenic character of PCA shown in this study. A paper by Rorabaugh and Norman (7) does show that salts of PCA appear less melassigenic than amino acids and that the latter decreased the solubility of sucrose.

Most basic nitrogen fractions have a negative correlation with purity. However, the correlation of betaine with purity is not significant. While betaine should appear antimelassigenic since it decreases the solubility of sucrose (10) it is likely that the variability in betaine content for the molasses in this study is so low that other factors obscure the real effect. For example, half of the betaine values are within 5% of the median value while over 70% are within 10% of the median. The three molasses having betaine values higher than 10% of the median have purities ranging from 61.21 to 59.01 while the two samples with the lowest betaine values have purities of 66.15 and 67.20.

Correlations of the variables with each other are shown in Table 2. It is extremely difficult to state in many cases if these relationships are valid or spurious. As we have shown earlier, the correlation of a number of variables with purity are dependent on their chloride content (meq of anions) or high correlation with chloride (meq of sodium plus potassium) and hence should be considered as spurious correlations. Of equal interest is the lack of correlation of certain variables with others: alkalinity of ash, meq of anions less chloride and nitrate and total weight of acids.

Dedek's (2) value of one for the ratio of sucrose over sodium plus potassium applies to the molasses samples discussed in this paper. The average value is 0.966 with a standard deviation of 0.106. A new ratio is presented here for consideration. The ratio of equivalents of sucrose to equivalents of anions is also close to one. Table 3 compares this ratio with Dedek's. Sucrose to anions has an average value of 1.029 with a standard deviation of 0.0876. The ratios found for Steffen molasses will be discussed later.

Steffen Molasses

Steffen molasses is defined as the molasses discard obtained from factory using the Steffen process. Usually foreign molasses from one or more straight houses is also processed with the factory molasses. A small portion of molasses may be discarded continuously or batches of molasses may be discarded when the

Table 3.—Comparison of the ratios of sucrose with anions and sodium plus potassium.

Straight house molasses			Steffen molasses		
Factory no.	meq sucrose/ meq anions	meq sucrose/ meq Na + K	Factory no.	meq sucrose/ meq anions	meq sucrose/ meq Na + K
1	1.017	1.023	21	1.074	1.083
2	1.029	.972	22	1.166	1.094
3	.938	.798	23	1.011	.952
4	.893	.773	24	1.185	1.314
6	1.078	1.110	25	1.367	1.216
7	.990	.967	26	1.231	1.165
8	1.145	1.080	27	1.031	1.020
9	.994	.875	28	.999	.936
10	1.031	.970	29	1.102	1.150
11	1.006	1.040	30	1.201	1.196
12	1.063	.936	31	1.052	.964
13	1.144	1.087	32	1.083	1.009
14	1.165	1.074	33	.995	1.170
15	1.020	.894	avg	1.1152	1.0976
16	1.078	.996	std. dev.	0.1097	0.1164
17	1.066	1.027			
18	.829	.806			
avg	1.0286	.9664			
std. dev.	0.0876	0.106			

purity of the returned calcium precipitate decreases to a particular value.

When we examine the correlations of the variables with Steffen molasses purity, shown in Table 1, we find a very unexpected situation. The correlations are very different from those found with straight house molasses. Variables that had a negative correlation with purity of straight house molasses may show a significant positive correlation with Steffen molasses purity. Variables showing a positive correlation with straight house molasses purity usually have a negative correlation with Steffen molasses purity. A substance that is melassigenic for one type of molasses should also be melassigenic for another type. The differences found cannot be due to a change in melassigenic properties but must be due to some other cause. The most probable cause is some change in the manufacturing process. Except for minor variations such as impurities in processing water, the impurities in straight house molasses come directly from the beets. This is not the case with Steffen molasses. Steffen molasses impurities arise from two major sources: (a) impurities from the new beets being added to the process and (b) impurities carried back by the calcium precipitate formed when dilute molasses is treated with calcium oxide. The discarded filtrate from the calcium precipitate will contain most of the soluble salts so the ratio of impurities to each other will be much different in this case than with fresh beets.

The impurities in the beets and calcium precipitate are

essentially the same in kind but are different in relative amounts. Hence, in the manufacture of sugar by the Steffen process we are mixing two different raw materials in varying amounts.

Because of these changes in operating procedures we do not obtain valid correlations relating the melassigenic properties of the variables to purity.

Since there are two sources of impurities, far fewer of the variables investigated show a significant correlation with each other than in straight house molasses. The correlations are generally of lesser significance.

The ratio of sucrose to meq of anions or sodium plus potassium is about 10% higher than for straight house molasses. During the calcium oxide precipitation of sucrose, reducing sugars and some sucrose are decomposed to acids. These are returned to the process as calcium salts. Generally sodium hydroxide or sodium carbonate is added early in processing to preserve alkalinity and remove excess calcium. Part I of this study shows that the sodium to potassium ratio is generally greater for Steffen molasses.

The best correlation is shown by purity and pH. The high pH samples have a significantly lower purity. Further study of this variable is desirable since no direct cause and effect relationship seems apparent to the authors. Reducing sugars are positively correlated with purity as would be expected because of their high correlation with pH.

Summary

Correlations of the non-sugars with purity have been calculated using percent of specific impurity in the impurities against molasses true purity. This method of calculation avoids the built-in spurious negative correlation obtained when calculations are made on the wet or dry basis.

The most important finding is the positive relationship between chloride content and purity. The results indicate that one pound of chloride carries between six and seven pounds of sugar into molasses.

Variables such as ash, meq of potassium plus sodium and meq of anions show a positive correlation with purity only because of their chloride content or high correlation with chloride. Total meq of sodium plus potassium less the meq of these ions present as chloride do not show a significant correlation with purity.

Many of the fractions containing nitrogen compounds show a negative correlation with purity which is probably due to a decrease in sucrose solubility in the presence of these compounds. These results are confirmed by comparisons using Belgium data.

Dedek's observation of a ratio near one for meq of sucrose to those of sodium plus potassium has been confirmed. A new ratio of meq of sucrose to anions is shown to be as reliable.

Melassigenic impurities in Steffen molasses do not show correlations with purity since the impurities are derived from two sources: processed beets and the calcium precipitate formed from straight house discard molasses.

Acknowledgments

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