The Relationship and Significance of Carbonate and Sulfated Ashes and the Approximate Salt Content of Beet Sugars, Sirups, and Molasses[1]

CHARLES A. FORT AND SAM BYALL[2]

The ash content of agricultural products and by-products of all kinds is such an ancient and common concept that in general it is accepted as being a rather definite measure of mineral content and degree of purity. Chemists have realized for 20 years that the simple carbonate ash does not give a true measure of mineral content of some products, although in other instances it is quite satisfactory. This discussion will be largely confined to sugar-beet products, but necessarily some of the general considerations will also have to be taken into account.

First of all, let us define the true mineral content and the theoretical carbonate ash as being synonymous and meaning the total inorganic elements or minerals plus the carbonate residue of organic salts. The actual determined carbonate ash from a given amount of mineral content is influenced by the composition of the original salts, the proportion of accompanying organic material, and the technique and temperatures used in ignition.

The presence of magnesium, and to a lesser extent that of calcium, in significant proportions, is especially likely to produce a misleading ash value. In most instances, magnesium occurs in the ash as the oxide, and frequently a portion of the calcium is also weighed as the oxide. This condition is very little improved by recarbonating, if the ash is again ignited at high temperatures. Wichmann has suggested that ignition after recarbonation should be at 250° C. or below the decomposition temperature of magnesium carbonate. He has also indicated that values so obtained may be higher than a true carbonated ash because of residual water of hydration or the presence of acid salts. A suitable method for obtaining a fully carbonated ash is still to be found, but even if found it still would not give a result representative of the true mineral content under certain circumstances which will be considered later. Some idea of the effect of magnesia on ash values may be had from the example of 2 products

with the same mineral content but consisting in the one case of 1 percent potassium sulfate and in the other case of 1 percent magnesium chloride; the corresponding ashes would be 1 percent and 0.42 percent, respectively.

With increasing ratios of carbonaceous material to minerals there occurs increasing decomposition and losses of sulfate and sulfite radicals and their substitution by the lighter carbonate radical. Taking a simple example again, if a sugar contained 100 parts per million of potassium sulfate the ash obtained would not be this amount but would approach 79 parts per million, the equivalent weight of potassium carbonate.

Further, there are variable losses of the chloride radical resulting from the substitution of the lighter carbonate radical. This condition is intensified if the ash has a low, natural alkalinity. It is these losses of sulfur compounds and chloride that make even a fully carbonated ash still below the true mineral content or theoretical carbonate ash as defined.

All this is entirely independent of the personal element in preventing mechanical and weighing errors and the losses of so-called organic sulfur and phosphorus. The object of these remarks is not to discredit confidence in ash values but to make it clear that they do not always represent the true mineral content nor bear any uniform relation thereto. The unfortunate part is that ash values are often used to define grades or to indicate purity of products which differ in salt composition as a result of agronomic conditions in the different areas where produced. Then products containing mostly minerals of the fixed type, such as potassium sulfate, will tend to show a high ash value and, therefore, a lower indicated purity than the product from an area where it has a high content of magnesium or organic salts which yield a misleading low ash. From actual analyses of commercial molasses, it is evident that some samples of lower ash are higher in mineral content than other samples of higher ash. So care should be taken when judging the mineral content or purity of products by ash determinations.

Sulfated ash content may be defined as the weight of the metallic bases as sulfates and phosphates. All the common acid radicals are replaced by the sulfate ion with the exception of the phosphate. In beet products following earbonation, phosphates are present only in traces and the sulfated ash of these products is therefore a direct comparative measure of the amounts of metallic bases present, for they are all weighed as sulfates. The sulfated ash is equal to or higher than the true mineral content, and part of its value as a determination lies in the fact that it does give a measure of the metallic bases on an almost uniform basis, while in carbonate ash the metallic

bases are weighed as an unknown mixture of oxides, carbonates, chlorides, sulfates, phosphates, etc. The sulfated ash has a further advantage in being relatively non-hygroscopic, thus can be weighed with more accuracy. It provides an excellent means of comparing mineral content of materials, even though it exaggerates this content somewhat in most cases.

There are certain points in regard to the determination of sulfated ash which should be mentioned: In general it is best to ignite the material until essentially free from carbon before sulfating. In special instances it is desirable to add sulfuric acid direct to the sample as a means of speeding up the ignition but the ash so made must be resulfated after it is free from carbon. Where the quantity of ash is high, it is advantageous to use an alcohol-sulfuric-acid mixture for sulfating rather than to add any water to the ash. This reduces the difficulties of re-introducing the ash into the muffle without losses due to decrepitation. Ignition after sulfating should be for 2 hours at 600° C. to insure complete transformation of acid sulfates. Only the central part of a muffle should be used, as temperatures at the front and back may be considerably below that desired, with subsequent high weights due to residual acid salts that escape decomposition.

It has been customary to deduct a particular proportion of a sulfated ash, most commonly 10 percent, to make an approximation of carbonate ash. If by carbonate ash we mean the determined carbonate ash, this procedure is especially misleading, but if we mean the true mineral content or theoretical carbonate ash, then, on the average it may be a fair approximation. There is, of course, no uniform correlation between sulfated ash and either determined or theoretical carbonate ash and the use of a factor is not really justified. If the original salts were principally sulfates and phosphates, then the carbonate ash and sulfated ash may be almost identical, while if the original salts are mostly organic, then the carbonate ash, both determined and theoretical, may be 20 percent or more below the sulfated ash.

We have previously defined mineral content and theoretical carbonate ash as the inorganic elements plus the carbonate residues from organic salts. Determined carbonate ash is variably below this value and sulfated ash usually above this value, for reasons already discussed. We have a fourth concept to consider, that of the salts themselves. Usually salt content is above sulfated ash. There are exceptions, for instance when the chloride content is high and again when the combined organic acid has a combining weight below 48, but in most vegetable materials the organic acids are generally complex and high in combining weight and chlorides do not predominate. In using carbonate ash as a means of judging purity of a product one may

be much in error. If the salts are principally inorganic, then the salt content and ash may be in fair agreement, but it is not likely. Since the salts present are usually high in organic salts, then certainly carbonate ash gives a very poor indication of purity. In one instance carbonate ash may represent that same amount of salts and in another case be the residue from double the quantity of salts. Thus, two products of equal quality as judged by carbonate ash may be widely apart in actual purity.

Total salts, including the organic salts, cannot be determined directly but they may at least be approximated. The combined organic-acid radicals are directly related to the true alkalinity of a carbonate ash. Under some conditions the total alkalinity of the ash may include that derived from the replacement of portions of the original chloride, sulfite and sulfate radicals by carbonate or oxide, so correction must be made for alkalinity derived from these sources.

Usually a titrated ash alkalinity is corrected on the basis of determinations of chloride, sulfite and sulfate on the original sample and determinations of chloride and sulfate on the ash. The modified procedure that we recommend involves the determination of the original chlorides, sulfites and sulfates as usual, then the sulfated ash and the sulfates of the sulfated ash. This eliminates only one determination, but the sulfated ash is essential for the calculation of total salts. The total sulfates content of the sulfated ash less the original sulfates and the sulfate equivalents of the original sulfites and chlorides is the value of the true alkalinity expressed as sulfate. In symbols this reads as follows:

True ash alkalinity as equivalent SO_3 =
SO_3 of sulfated ash—(Orig. SO_3+Orig. SO_2 x 1.25+Orig. CI x 1.13)

The value obtained may be used as it is, for expressing comparative amounts of organic-acid radicals, or it may be calculated to the equivalent of the known or probable organic acid present. In the case of sugar-beet products, while many organic acids have been isolated and identified, it would be difficult indeed to determine them on individual samples, so just to make the picture somewhat more realistic, it seems proper to select arbitrarily a reasonable value for the average combining weight of the organic acids involved. The assumed combining weight that will be used in this discussion is 80, for the organic acids remaining in the products following carbonation are believed to be relatively complex and to a considerable extent nitrogenous. (Oxalic acid, which has a low combining weight, is largely eliminated in juice clarification.) Using this 80 combining weight, then the figure for organic-acid radicals is equal to twice that for the true ash alkalinity, as SO_3.

It is now possible to make an approximation of the total salts from the data on hand from this procedure of determining true ash alkalinity. The calculation is as follows:

Total salts=Sulfated ash+True alkalinity as SO_3 x 0.8—
(Orig. CI x 0.35+Orig. SO_2 x 0.50)

Similarly it is possible to calculate the theoretical carbonate ash or mineral content as defined earlier, thus:

Theoretical carbonate ash or true mineral content =
Sulfated ash—(True alkalinity as SO_3 x 0.45+Orig. CI x 0.35
+ Orig. SO_2 x 0.50)

It may be noticed that the compounds of phosphorus have been left out of consideration. There are some reasons for this: First, in sugar-beet products following juice clarification phosphates are present only in traces; second, the exact form in which phosphorus is combined in ashes is uncertain, as yet, but it appears likely that the combining weight of the phosphorus-compound radical may be reasonably close to that of the sulfate radical so that, even if phosphates are ignored, the calculations of total salts and total minerals may not be significantly in error. Also, it should be realized that in these proposed calculations the normal neutral salts are assumed.

We now consider the relationship of determined and theoretical carbonate ash, sulfated ash and total salts on the basis of some simple composition. Assuming mixtures of potassium salts consisting of (1) sulfates and organic salts, and (2) chlorides with organic salts, we can make two sets of typical curves.

Figure 1 is for different proportions of sulfates and organic salts with a constant total potash content. We note first that since the total potash content is taken as constant, then the sulfated ash must also be constant. With increasing proportions of organic salts the theoretical carbonate ash decreases to a low representing 100 percent potassium carbonate. The determined carbonate ash, where the ratio of carbonaceous material to minerals is high as in sugars, will approach a line drawn at the potassium-carbonate level representing complete replacement of the sulfate radical by carbonate. Note that under any condition the determined carbonate ash approaches the theoretical ash as the proportion of organic salts increases. The total salts, using the 80 combining weight for the organic radical, increase rapidly so that the determined ash becomes a very poor indicator of purity when organic salts are high.

Taking the example of mixtures of potassium chloride with organic salts, figure 2, the same general situation holds. However, due to the weight of the chloride being lower than the sulfate, the curve
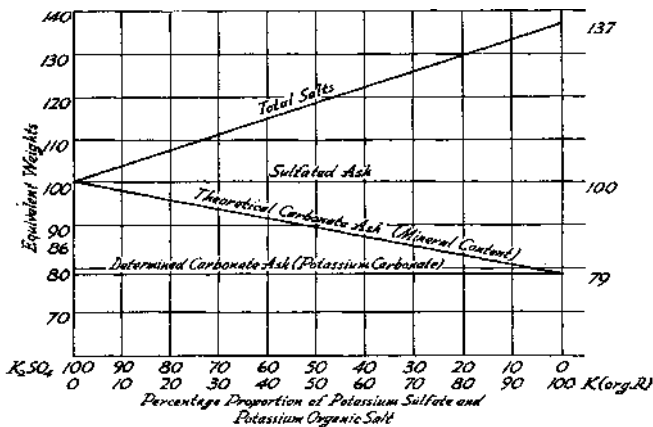
Figure 1.—The relationship between ash values and salts for mixtures of potassium sulfate and potassium organic salt with total K_2O constant.
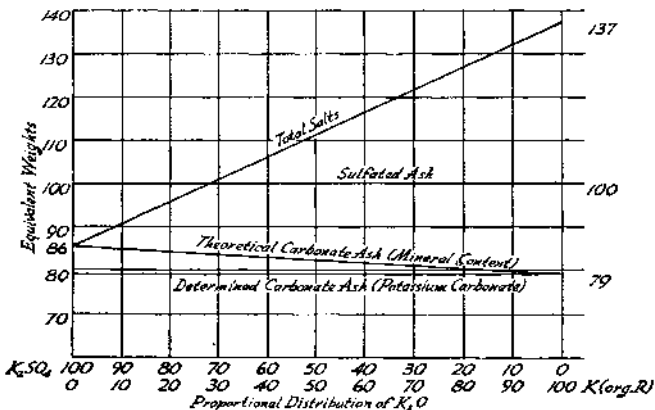

Figure 2.—The relationship between ash values and salts for mixtures of potassium chloride and potassium organic salt with total K_2O constant.

for total salts starts below that for sulfated ash and as organic salts increase, the former crosses the latter. Further, the smaller differences in weight between chloride and carbonate make the discrepancies between theoretical and determined carbonate ash small even if all the chloride were lost in ashing. Sulfites present a similar picture intermediate between the chloride and sulfate curves. In all three examples or any combination thereof the total salts increase progressively with increase in organic salts, attaining a point 37 percent above sulfated ash and 72 percent above determined and theoretical carbonate ash. As many sugar products are high in organic salts, these curves show how poor an indication of their purity is given by ash determinations.

We can now take a look at some actual determinations made on beet sugars, sirups, and molasses. Table 1 gives the average figures for 5 sugars low in organic salts in comparison with those for 5 sugars high in organic salts, and also the average figures for the 83 sugars from the different factories for the 1940 campaign. Analytical methods are not so perfected that these values may be considered absolute, but it is felt that they represent the true trends. Note that the determined carbonate ashes are very low compared with the theoretical carbonate ash, indicating a nearly complete loss of sulfur compounds and chloride. Analytical tests on ashes showed this to be true in the case of sulfur compounds; tests were not made for chlorides. The smaller difference between the determined and the theoretical carbonate ashes in the example where the organic salts are high is in line with the curves just shown. You will note too that the group of sugars with the high organic-salt content gave a lower, determined, carbonate ash than the other group of sugars which had a slightly lower, total, salt content. The latter part of the table shows the pro-

Table 1.—Ash and salt relationships on beet sugars.

	Average of 5 sugars with low organic salts	Average of 5 sugars with high organic salts	Average of 83 sugars 1940
Percentage of organic salts on total salts	8	72	47
	percentage	percentage	percentage
Determined carbonated ash	0.0087	0.0071	0.0098
Theoretical carbonated ash	0.0106	0.0080	0.0112
Sulfated ash	0.0112	0.0093	0.0125
Calculated total salts	0.0110	0.O115	0.0141
Relation to theoretical carbonate ash			
Determined carbonated ash	—18	—11	—13
Sulfated ash	+6	+16	+12
Total salts	+ 4	+44	+26

Note: Organic salts calculated on basis of corrected ash alkalinity and equivalent organic-acid radical of 80 combining weight.

portional differences between the values found.   Especially note the large proportional differences between total salt content and the ash values.   The effect of chlorides in the calculation of total salts is evident in the sugars of low organic-salt content where the estimated total salts are a shade below sulfated ash.

In table 2 are shown similar data for thick juices or sirups. Since only 15 samples were studied, the contrasts are not so great as for the sugars, but they indicate the same trends.   Because of the much lower ratio of sugar to ash, the differences between determined and theoretical carbonate ash are small.   Analytical determinations on the ashes confirmed the fact that the losses of sulfur compounds and chloride had been low.   This better agreement would also be expected because of the generally high proportion of organic salts.   The contrast between salt content and carbonated ash is greater than for the sugars.

Table 2.—Ash and salt relationships on thick juices.

	Sirup with lowest organic salts	Sirup with highest organic salts	Average of 15 sirups
Percentage of organic salts on total salts	70	92	79
	percentage solids	percentage solids	percentage solids
Determined carbonated ash	2.151	2.170	2.338
Theoretical carbonate ash	2.240	2.212	2.398
Sulfated ash	2.652	2.762	2.194
Total salts	3.218	3.696	3.676
Relation to theoretical carbonate ash			
Determined carbonated ash	— 4	— 2	— 3
Sulfated ash	+ 18	+25	+22
Total salts	+44	+67	+ 63

In table 3 are given the corresponding values as determined on non-Steffen beet molasses.   Theoretical and determined carbonate ash agree even more closely than on the thick juices, and again the contrast between ash determinations and salt content is very great.

These sugars, sirups, and molasses are not directly comparable, since they are not from the same factories, but one trend in the figures is so pronounced that it is likely to hold true for the products of individual factories.   This is the generally lower proportion of organic salts in the sugars as compared with the sirups and molasses. Apparently the sugar in crystallizing takes up the mineral salts to a much greater degree than the organic salts, in spite of the fact that the latter are in greater concentration in the sirups.   More comprehensive studies along this line are planned.

Table 3.—Ash and salt relationships on beet molasses (non-Steffen).

	Molasses with lowest organic salts	Molasses with highest organic salts	Average of 15 molasses
Percentage of organic salts on total salts	60	94	77
	percentage solids	percentage solids	percentage solids
Determined carbonated ash	19.11	12.24	14.09
Theoretical carbonated ash	10.00	12.23	15.03
Sulfated ash	23.75	15.27	18.40
Total salts	26.98	20.72	22.56
Proportional relation to theoretical carbonate ash			
Determined carbonated ash	— 4	± 0	— 2
Sulfated ash	+ 19	+ 25	+ 22
Total salts	+36	+69	+ 50

In conclusion, some comments should be made on conductivity-ash factors. Considering the variable relation of determined carbonate ash to mineral content and salts, it is evident that, with everything else equal, conductivity cannot be expected to correlate perfectly with ash determinations. Add to this the varied effect of different ions on conductivity and it becomes really remarkable that a reasonably uniform correlation would be possible. As you know, there is a fair degree of uniformity even in the simple ash-conductivity factors for beet sugars which is improved when based on sulfated ash. The correlation of conductivity with estimated total salts showed about the same variability as found in the case of carbonate ash.

That the relatively low conductivity of organic-acid radicals affects the conductivity-ash factors is shown in the data obtained this past season. Ten sugars with low proportions of organic salts gave an average sulfate ash-conductivity factor of about 225 when compared with 10 sugars of high organic salts having an average factor of 200. The corresponding carbonate ash-conductivity factors were respectively 290 and 250. Sirup and molasses conductivities indicated this same trend. On all products some individual samples gave factors which were extreme without any explanation being apparent from the composition found.

Summary

1. Theoretical carbonate ash or mineral content is defined as the total content of inorganic elements plus the carbonate residues of organic salts.

2. Determined carbonate-ash values are usually lower than the theoretical; the amount of the difference is variable both as to weight and proportion.

3. The most pronounced differences occur when (a) magnesium content is high, (b) the ratio of carbonaceous material to ash is high,

and (c) the ash alkalinity is low. Magnesium is commonly present in the ash as the oxide, unless the ignition following re-carbonation is at a relatively low temperature. Sulfates and sulfites are largely lost and replaced by carbonates when the product tested is extremely low in ash, as are sugars. Chlorides are lost to a variable degree and substituted by carbonates unless large excesses of free alkali are present. The losses of sulfur compounds and chlorides make even a completely carbonated ash low as compared with the theoretical.

4. The agreement of the determined and theoretical carbonate-ash values is improved as the proportion of organic salts increases.

5. Sulfated ash is an almost perfect measure of the amounts of metallic bases present. It is the same as, or higher than, the theoretical carbonate ash and nearer to the salt content, but not uniformly correlated with either.

6. When the proportion of organic salts is high both determined and theoretical carbonate ash give a poor indication of the purity of the product tested. Sulfated ash is better but still too low.

7. Combined organic-acid radicals, theoretical carbonate ash, and total salts may be calculated on the basis of sulfated ash and corrected ash alkalinity. A modified method of determining true ash alkalinity has been outlined.

8. The proportion of organic salts to inorganic is much lower in beet sugars than in the sirups from which they are crystallized.

9. Conductivity-ash factors are much influenced by the organic-salt proportion.

10. The approximated salt content gives a truer indication of product purity than any modification of an ash determination.

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