SUGAR-END MANAGEMENT IMPLICATIONS FOR THE METHOD CHOSEN TO MEASURE DRY-SUBSTANCE

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Introduction:

The measurement dry substance (DS) is important in sugar-end management. Dry substance is the sum of all dissolved and suspended solids in a solution or massecuite. Its value is used to calculate a host of parameters important to controlling and evaluating crystallization. There are a variety of methods for measuring it including refractive index (RDS), oven dry (ODS), sand dry (SDS) and Karl Fisher titration (KDS).

RDS is most often used because of its convenience. In the laboratory it provides a simple, quick test that is highly reproducible. All DS determined by RDS is converted to the Brix scale, which is the correlation between DS and refractive index of pure sucrose solutions. RDS gives the most accurate DS values for high-purity solutions. Pure solution containing common nonsugars such as potassium acetate and sodium glutamate give Brix values that are > 20% in error of their true DS[1]. The processing of beets containing different ratios of various nonsugars can give different RDS values for the same DS.

Drying a sample in the oven until all the moisture has been driven off is straight forward. Like determining the RDS oven drying is highly reproducible, but it takes several hours and requires more analyst time and skill. The accuracy of this method is in question because of two problems 1) volatile compounds may be driven off with the water and 2) as samples dry, they harden on the outside first, making it difficult for the moisture under the hard outer crust to escape. To get around these problems two modifications to the oven drying method are employed. The first is to spread the sample out over sand to give a larger surface-to-bulk ratio. The second is to reduce the temperature of the drying, including drying under vacuum. Both of these modifications will aid in the drying. The second also reduces the thermal breakdown of nonsugar components to volatile compounds during drying.

The general equations for Karl Fisher titration are given below where RN is a base (Equations 1 & 2). This method uses water and iodine in a 1-to-1 ratio so by measuring the consumption of iodine, the amount of water can be measured. KDS will give errors if there are compounds that react with the various reagents, especially iodine. In sugar solutions the components that react are low in concentration relative to water and should not materially affect the result. As an analytical method, it takes specialized equipment and reagents that are affordable and readily available. The method is much quicker than oven drying but it takes more skill. Only a minute amount of water is being measured, so the leaks in the apparatus and high humidity can give a negative error in DS.

$$CH_3OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3 \qquad \text{Eq. 1}$$

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4\ CH_3 + 2\ [RNH]I \qquad \text{Eq. 2}$$

Objective:

The purpose of this paper is to look at the DS values determined for molasses and low-raw massecuite with the different methods, then use these values to see how these differences propagate through some example calculations for purity and nonsugar-to-water ratio.

Materials and Methods:

A weekly production molasses composite is made by adding 150 mL of four daily and 450 mL of the week-end composite samples together. These composites are made by adding about 35 mL of production molasses every four to a non-refrigerated container. The low-raw massecuite samples were collected as the massecuite exited the continuous low-raw pan.

Determination of RDS: 35 grams of molasses was diluted to 200 grams with DI water. The diluted sample was filtered with filter aid through a # 413 filter paper. The RDS of the diluted sample was read on a Rudolf refractometer equipped with a flow-through cell. The sugar content of this sample was determined by polarimetery and HPLC.

Determination of ODS: 1 to 1.5 g of undiluted sample was smeared on a 70 mm diameter aluminum capsule with lid. The sample was dried in a forced draft oven at 106°C for six hours, placed in a desiccator and cooled for 30 minutes before weighing. The difference in weight between the capsule and sample before and after drying was the water in the original sample.

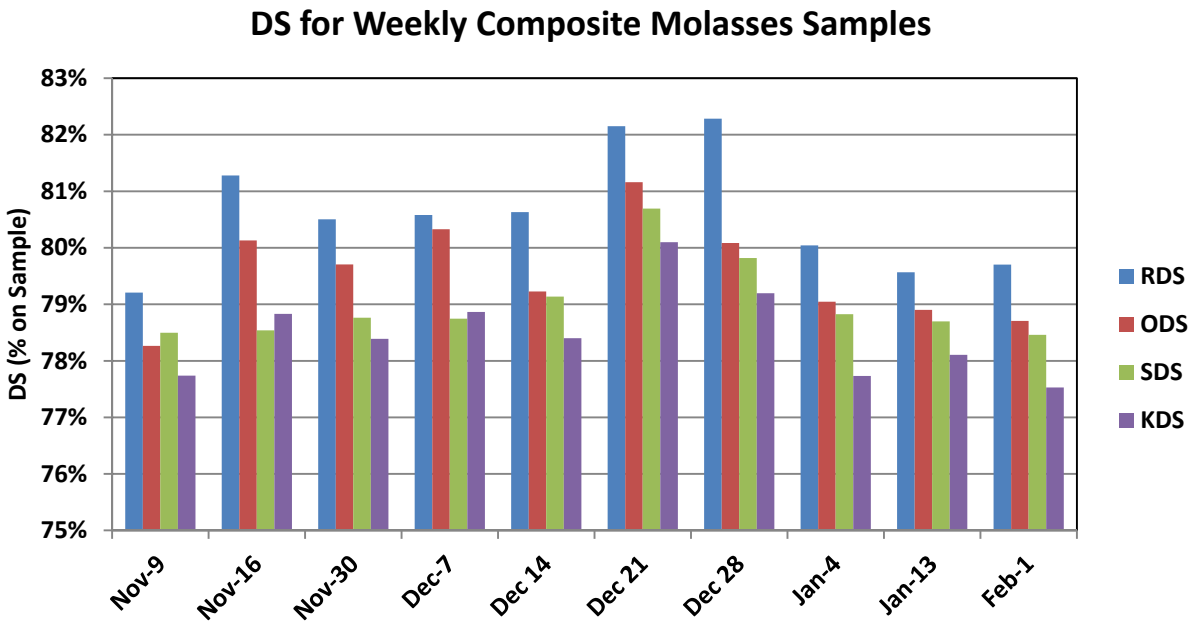
Determination of SDS: 130 g of sample was diluted to 200 g with DI water targeting about 50% DS. 25 to 30 g of sea sand was placed in a 52 mm diameter aluminum capsule with lid. 1 to 1.5 g of the diluted sample was used. A small glass rod was used to mix the sample and sand. The sample was placed in a convection oven at 100°C for 10 hours then placed in a desiccator and cooled before weighing. The difference in weight between the capsule with sand and sample before and after drying was the water in the original sample.

Determination of KDS: 130 g of molasses was diluted to 200 g with DI water targeting about 50% DS. 1 mL of the diluted sample was drawn into a plastic syringe for dispensing into the Karl Fisher titration vessel. Approximately 0.04 g of diluted sample was used for each Karl Fisher titration. A w/w sugar solution was used to determine the titer of the Karl Fisher reagent. The water of the diluted sample determined by titration was multiplied by the dilution factor to calculate the water in the original sample.

Results and Discussion:

The DS results for the molasses composite samples are shown in Figure 1. The RDS consistently gave the highest value. The ODS was the next highest in all but the November 9 sample where the SDS gave a higher reading. The SDS was greater than the KDS in all but two samples, November 16 and December 7.

For each sample the difference between the DS results from each method was determined. The average of the difference between each method was determined. The individual differences were then compared to twice the standard deviation of the average and any that were greater were thrown out. The average was then recalculated. The results are shown in Table I.



Errors in measured values are a combination of the random and systematic errors. By averaging the results of multiple samples, random errors will be reduced by the square root of the number of samples averaged. The averaged differences will give a more accurate measure of the systematic errors between the methods.

Table I: Average Difference in the DS Values by Analytical Method for Molasses Composite Samples.

	RDS	Oven Dry	Sand Dry
Oven Dry	0.96%		
Sand Dry	1.59%	0.55%	
Karl Fisher	2.11%	1.07%	0.53%

Purity calculated from DS determined by each of these methods will be different. Table II shows the purities that would be seen if the DS is determined by refractive index is 60 and it has 48% sucrose. Purity is the ratio of sugar to DS (Equation 3). The relative error in the purity is root mean square of the relative errors of the sugar and DS values (Equation 4)[2]. The relative error of the purity will be at least as big as the relative error in either of the components. The differences of the DS values seen in the molasses samples do have a material impact on the calculated purity.

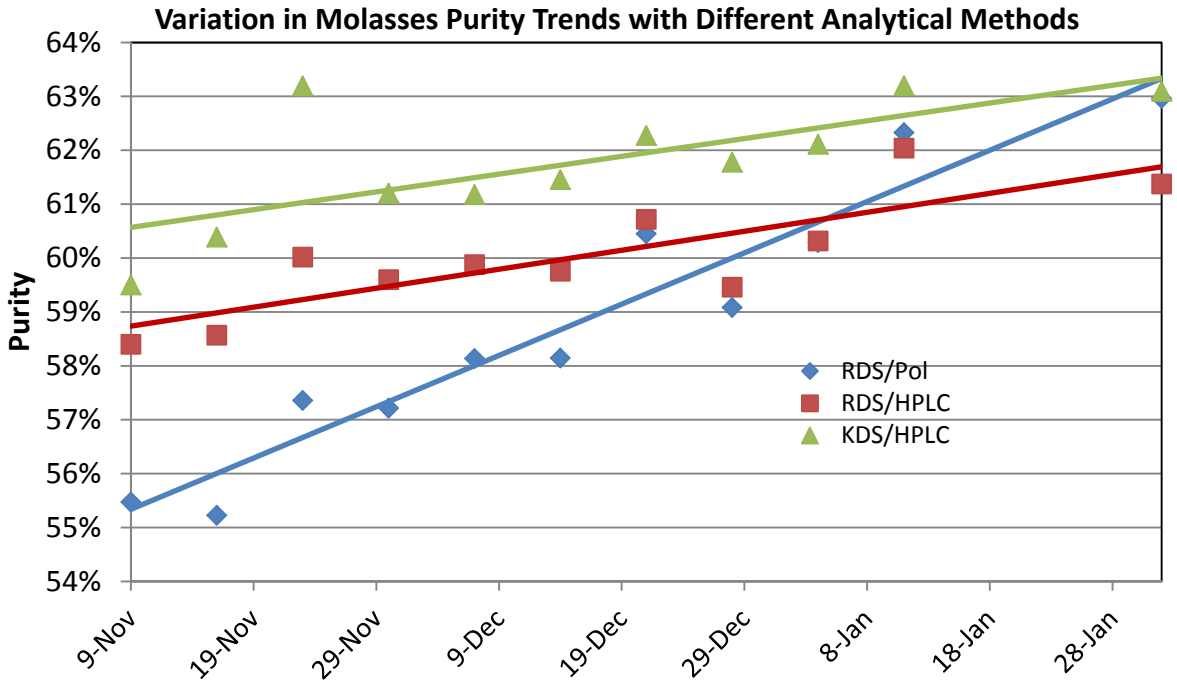
$$Purity = \frac{[S]}{[DS]} \qquad \text{Eq. 3}$$

$$\frac{\varepsilon_{[P]}}{P} = \sqrt{\left(\frac{\varepsilon_{[DS]}}{[DS]}\right)^2 + \left(\frac{\varepsilon_{[S]}}{[S]}\right)^2} \qquad \text{Eq. 4}$$

Table II: Calculated Molasses DS and Purity Based on a Molasses of 80 Brix and 60 Purity

	Dry Substance	Purity
RDS	80.0%	60.0%
Oven Dry	79.0%	60.7%
Sand Dry	78.4%	61.2%
Karl Fisher	77.9%	61.6%

Figure 2 shows trends by date of the weekly composite molasses sample purities calculated in three different ways. The blue diamonds show the purity calculated using RDS and polarization for sugar (apparent purity). The red squares show the trend with purity calculated using RDS and high performance liquid chromatography (HPLC) for sugar are used. The green triangles show the trend in purity when KDS and HPLC are used. The best-fit, least-squares linear regression lines of purity against date are also shown.



The choice of analytical methods for both the DS and sugar has an effect on the calculated purity. All three trends show increasing molasses purity through the campaign. The choice of RDS or KDS changed the intercept of the trend but has negligible effect on the slope. The choice of pol or HPLC changed both the slope and the intercept. Taken together, these suggest that there is a real increase in the purity of the molasses as campaign progressed and it was not just an artifact of the analytical methods selected.

Much of the difference between the RDS/pol purity and RDS/HPLC purity can be explained by the increase in raffinose as the beets sat in the storage piles. The raffinose in the molasses

increased from 0.8% to 3.7% during this period. It is unlikely that a change in the ratio of nonsugars would have the same effect on both the RDS/HPLC and KDS/HPLC purities, as RDS and KDS are affected differently by different nonsugars.

The question of which DS method is unresolved by looking at the purity values or trend. From this data, both the HPLC/RDS and HPLC/KDS purities give good information when trying to look for changes during campaign. With molasses exhaustion a primary target of sugar end operations, it appears that either could be used as long as the target molasses purity is determined with the same DS determination.

The nonsugar-to-water ratio (NS:W) is another important sugar-end parameter that is calculated from DS. It is used to determine the potential for molasses exhaustion in low-raw massecuite. A high NS/W means greater potential for molasses exhaustion as long as it does not get too high. Both the NS and W values are determined using DS (Equations 6 and 7).

$$\mathrm{NS{:}\,W} = \frac{[NS]}{[W]} \qquad \text{Eq. 5}$$

$$[\mathrm{W}] = 1 - [DS] \qquad \text{Eq. 6}$$

$$[\mathrm{NS}] = [DS] - [S] \qquad \text{Eq. 7}$$

The equations for the propagation of the errors in the measured values to the calculated W and NS values are shown below (Equations 8 and 9). The absolute error for W is the same as the absolute error for DS. Since W in low-raw massecuite is only a fraction of the DS, its relative error will be significant. The error in the NS will be a combination of both the errors in the DS and S measurements. Though the nonsugar value is not as small as the water is relative to DS, it is small enough that the relative errors in both the DS and S measurements will be magnified in the calculated NS value

The error in NS:W contains the DS in each term. Equation 10 shows how the error in DS propagates through the relative error for NS:W. Equation 10 tells us that the relative error in NS:W will be at least as large or larger than the relative error in either of the components.

$$\varepsilon_{[W]} = \varepsilon_{[DS]} \qquad \text{Eq. 8}$$

$$\varepsilon_{[NS]} = \sqrt{\varepsilon_{[DS]}^2 + \varepsilon_{[S]}^2 - 2\varepsilon_{[DS]}\varepsilon_{[S]}} \qquad \text{Eq. 9}$$

$$\frac{\varepsilon_{NS:W}}{NS:W} = \sqrt{\left(\frac{\sqrt{\varepsilon_{[DS]}^2+\varepsilon_{[S]}^2-2\varepsilon_{[DS]}\varepsilon_{[S]}}}{[NS]}\right)^2 + \left(\frac{\varepsilon_{[DS]}}{[W]}\right)^2} \qquad \text{Eq. 10}$$

A low-raw massecuite sample was obtained from the exit of the continuous low-raw pan at SMBSC and the RDS (93.04%), and KDS (90.69%) were determined. If it is assumed that the KDS is the true DS and the RDS is in error, then the error and relative errors in the DS and W contents are shown in Table III. The relative error in the DS measurement is small at only 2.6%. However, this error propagates through to NS:W as a 27% relative error. In this example it is assumed that there was no error in the sugar measurement. If an error in the sugar measurement is included the NS:W relative error would be somewhat larger.

Table III: Propagation of Error from RDS Measurement to DS and W

	RDS	KDS
Dry Substance		
value	**93.0%**	**90.7%**
ε	**2.3%**	

$\varepsilon_{Relative}$	2.6%	
Water		
value	7.0%	9.3%
ε	2.3%	
$\varepsilon_{Relative}$	25%	
Nonsugar		
value	23.9%	21.6%
ε	2.3%	
$\varepsilon_{Relative}$	9.8%	
NS:W		
Value	3.4	2.3
ε	0.93	
$\varepsilon_{Relative}$	27%	

Many of the random errors can be reduced through good sampling protocols and laboratory technique. Random errors can be minimized by averaging the results of the multiple samples, but this does not help when calculations are conducted on single samples, as is often required in the sugar factory.

It appears that there are definable systematic differences in the DS values determined by the various methods. As shown with the purity and NS:W examples, these differences can propagate and magnify into calculated parameters used to control the sugar end. The differences in nonsugars seen by different factories or by a single factory in different seasons or different periods during a single campaign may change the results from the different methods differently. Caution should be exercised when using "book" target values for many of the calculated parameters used to control sugar end operations, even targets that have been determined in the past for a specific factory.

Literature Cited:

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2. Carlson. J.L.; Golovanoff. G.W.; Kubat. K. A. Proceedings from the 27th Biennial Meeting of the American Society of Sugar Beet Technologists, 1993. p 42