Evaluation of Emerging Technologies: Importance of Correct Analytical Procedures

Kochergin, Vadim*, Stephanie Olmstead, William Jacob
Amalgamated Research Inc., 2531 Orchard Dr. E., Twin Falls, ID 83301

Abstract

Development of new technologies often requires revisiting analytical methods used routinely for monitoring factory performance. For example, introduction of membrane filtration or chromatography in both the beet or cane sugar industries will affect the quality of processed juices and syrups. Conventional analytical methods work well for comparison of the results for established technologies. The methods specific to a certain component of a solution are less affected by technology change. However, the bulk methods, such as refractometry, polarimetry, spectroscopy, etc., reflect the cumulative contribution of various components. Therefore, for example, the same purity or color of a solution may result in different processing characteristics of juice or syrup and different quality of the final product. Examples are discussed showing the differences in analysis of color, hardness, pol, dextrans, etc. in case of introduction of membrane and chromatographic technologies.

Introduction

Reliable analytical methods are essential for efficient operation of any production facility. The importance of this issue in the sugar industry was emphasized by creation of the International Commission of Uniform Methods of Sugar Analysis (ICUMSA) in 1897. Analysis of product streams in the sugar industry has been continuously improving for many years. Development of new technologies always calls for careful evaluation of the available analytical methods. The increasing interest in the membrane and chromatographic technologies spurred research efforts in both the beet and cane sugar industries. Mistakes in method selection and interpretation of analytical data may give misleading information about a new process.

Analytical methods can be conditionally divided into specific (targeting a single component in the solution) and non-specific, measuring a certain characteristic of a solution, such as dry substance, color, etc. The non-specific methods, such as refractometry, polarimetry, spectroscopy, etc. reflect the cumulative contribution of various components and are most affected by changes in processing methods. The purpose of our paper is to illustrate how the interpretation of analytical data affects the testing results and material balance calculation of the new processing procedures.

Suspended solids analysis

The most commonly used method of dissolved solids analysis in the sugar industry is based on refractometry (RDS). The method is known to be quite accurate in the absence of suspended solids or even in the presence of a small amount. It is not very clear to what extent the accuracy of the refractometric method depends on the concentration of suspended solids in a sample. For most practical purposes in the conventional processes it is assumed that suspended solids do not significantly affect RDS.

We have carried out a set of tests to verify the validity of this assumption. Samples of raw juice, membrane feed and concentrate were taken at different times during campaign. The RDS measurements were compared for 35 unfiltered samples and the same samples filtered through 0.45 um paper. A Bellingham-Stanley RFM 81 refractometer was used in all tests. Very rarely the readings came out the same for filtered and unfiltered samples, however, the difference was not consistent. The sample RDS measurements for various streams are shown in Table 1. Statistical analysis was performed to evaluate the significance of readings between filtered and unfiltered samples. The difference was found to be insignificant for samples of membrane feed with the lowest amount of suspended solids. In two other cases the difference was statistically significant. The absolute error in RDS determination may be as high as 0.88 for a 15% DS sample. Therefore, the oven-drying method was chosen for the samples with a high concentration of suspended solids. It is noteworthy, that the oven drying method gave consistently higher numbers when compared with either filtered or unfiltered samples.

Table 1
Effect of Suspended Solids on RDS Measurement

	Feed raw juice	Membrane feed	Membrane concentrate
Approximate suspended solids content, PPM	5,000-6,000	1,000-1,500	5,000-10,000
Average difference between unfiltered and filtered samples	0.026	0.003	-0.12
Percent deviation from filtered sample	0.18	0.02	0.78
Maximum absolute difference between the samples	0.10	0.18	0.88

Analyzing the RDS of raw juice samples is sufficient for the purposes of a conventional sugar factory. However, if a membrane filtration process is considered, an additional method of suspended solids analysis is required to make sure that the process material balance converges. A correction for suspended solids will be necessary if a material balance is based on RDS measurements.

Table 2
Estimate of sucrose balance discrepancy if suspended solids are neglected

	Based on dissolved solids	Corrected for suspended solids
Raw juice purity	88	88
RDS	16	16
Suspended solids flow @0.5% concentration, tpd	–	43.2
Raw juice flow, tpd	8640.0	8596.8
Sucrose in raw juice, tpd	1216.51	1210.43
Difference in sucrose, tpd	–	-6.08
Difference, $/campaign*	–	486,400

* 160 days campaign, $500/ton sugar

Data in Table 2 show that neglecting suspended solids in the raw juice stream results in a significant discrepancy of a sucrose balance. Since RDS measurement does not account for suspended solids, they should be subtracted from the total juice flow. Otherwise, the sucrose content in the raw juice will be overstated. Such error may significantly affect conclusions about the feasibility of a new process.

Apparent purity

Apparent purity of sugar solutions is calculated as a ratio of solution pol to the concentration of dry substance. It is well known that apparent purity does not account accurately for the amount of sucrose in the solution due to the presence of various amount of optically active components. However, polarimetry is still used routinely for daily measurements, especially in the cane sugar industry. When applied to new technologies, the method may lead to some erroneous conclusions on process performance.

A discussion about potential purity increase when raw beet juice is subjected to ultrafiltration may serve as a good example of such controversy. In the early experiments on membrane filtration permeate purity reportedly increased by more than 3-4 points. This purity rise was comparable to traditional juice purification; therefore, the goal of many researchers was to use membrane micro- or ultrafiltration as a replacement for conventional juice purification schemes. It is difficult to conclude today what the reason was for such optimistic results. Analysis of true purity by various researchers using several more specific methods shows that only a small purity increase can be expected.

Table 3
Effected of RDS Measurement on Apparent Purity
(Molasses and Raw Juice)

0.5% deviation in RDS measurement				
Pol	0.35	0.35	0.13	0.13
RDS	60.0	60.3	15.0	15.08
Apparent Purity	58.3	58.0	86.7	86.2
Difference	***0.29***		***0.43***	
0.1 point deviation in RDS measurement				
Pol	0.35	0.35	0.13	0.13
RDS	60.0	60.1	15.0	15.1
Purity	58.3	58.2	86.7	86.1
Difference	***0.10***		***0.57***	

Pol of the solution is always measured on filtered samples. A small deviation in RDS reading due to the presence of suspended solids may cause significant differences in apparent purity determination. The effect of a relatively small error in RDS measurement on apparent purity reading is illustrated in Table 3. Obviously the effect is more pronounced for high purity and low DS solutions, such as raw juice.

Color

According to the ICUMSA procedure color value is calculated based on the absorbance at 420-nm wavelength at pH 7. Obviously, multiple combinations of colorants may result in the same cumulative contribution to absorbance. In a conventional process the color value can be used to predict the processing characteristics of a certain juice or syrup. Rules of thumb have been developed that allow estimating the color transfer from syrups to the final sugar. Approximate color transfer ratios corresponding to various processing schemes are listed in Table 4. Low values of color transfer ratio are indicative of better purification (decolorization) methods. It is interesting that regardless of the color values of feed syrup, the color of final sugar in different processing schemes may be similar. The difference between sugar crystallized from standard liquor or chromatographic extract may serve as a good example. M. Godshall [1] indicated that the difference in color transfer ratios might be attributed to the concentration of high-molecular weight components in the syrups. The effect of membrane filtration on the quality of final product in the cane sugar industry confirms this suggestion. Since a new process, such as membrane filtration or chromatography, affects the molecular composition of a sugar solution, the existing rules of thumb need to be revisited.

Table 4
Color transfer ratios for various processing schemes

Process	Syrup pretreatment	Syrup color, ICUMSA	First strike sugar color ICUMSA	Color transfer ratio *100
Cane mill (conventional)	Coagulation, Settling	15,000	3,000 (unwashed)	20.0
Cane refinery	Affination , filtration, decolorization	300	10 (washed)	3.3
UF and NF [2]	UF/NF	3,590	304 (unwashed) 46 (washed)	8.5 1.3
Ultrafiltered cane clarified juice [3]	Ultrafiltration	15,000	600	4.0
Beet process (conventional)	Chemical treatment, DE filtration	3,000	30 (washed)	1.0
Chromatographic extract from beet molasses	Conventional and chromatography	6,000	30 (washed)	0.5
Chromatographic extract from cane clarified juice [4]	Ultrafiltration and chromatography	4500	30 (washed)	0.7

Hardness

Titration with EDTA for total hardness measurement is another "bulk" method that may be affected by introduction of new technologies. This method measures the concentration of calcium and magnesium in a sugar solution. Usually most of the magnesium is removed in a conventional lime purification process; therefore, the method works reliably for a conventional process. In a lime-free process (currently under development) the calcium-to-magnesium ratio is quite different from a conventional process. Although the EDTA titration may give results similar to the conventional process, magnesium ion will be prevalent. More specific methods may be required to accurately evaluate the composition of divalent ions. Neglecting such differences may lead to wrong conclusions about scaling effect in evaporation, juice softening and molasses exhaustion (magnesium has much lower melassigenic coefficient than calcium).

Dextrans

Removal of dextrans from solutions is critical for both beet and cane sugar manufacturing. It is not uncommon that a factory processing capacity is reduced by half due to poor storage of beets or harvesting conditions of cane. Dextrans are also known to adversely effect the quality of final sugar. The level of dextran removal may make membrane filtration more or less attractive for sugar technologists. The data from recent membrane testing spurred discussion on the efficiency of dextran removal. Our data showed significant discrepancy between the dextrans analyzed by the Roberts method and the haze method. The haze method recommended by ICUMSA is apparently more sensitive to high molecular weight dextrans. It usually shows 100% dextran elimination across a UF membrane with about a 100 kD molecular weight cutoff. The Roberts method, however, always shows the presence of some dextran in membrane permeate. It is outside the scope of the current paper to discuss the benefits and shortcomings of each method. However, it is a good illustration how correct selection of an analytical method may affect the decision about implementation of a new technology.

Additional methods

Introduction of new technologies may not only require reevaluation of the existing analytical techniques but also call for additional methods specific for new unit operations. These methods may not be a part of routine analysis in future operations but are definitely required for process evaluation and development. For example, the concentration or particle size analysis of suspended solids in the solutions is rarely or never performed. Literature definitely lacks this information, thus disallowing the technologists to make correct decisions concerning applicability of various solid-liquid separation methods. It is even more surprising taking into account that filtration, flocculation and clarification are key processes used in both cane and beet sugar industries. Even when membrane performance is evaluated the concentration of suspended solids is rarely mentioned. Lack of this information makes comparison of the flux through the membranes virtually impossible.

Acknowledgements

The authors are grateful to D. Eugene Rearick for his helpful comments.

References

1. M. Godshall, e.a., The nature of colorant, Proceedings of SPRI meeting, April 9-12, 2000, Porto, Portugal, pp.122-137.
2. Saska, M., e.a., Sugar J., November 1995, pp.19-21.
3. Kwok, R., Ultrafiltration/softening of clarified juice, Proc. SPRI Workshop on separation processes in the sugar industry, 1996, pp. 87-99.
4. Kochergin, V., M. Kearney, e.a., Chromatographic desugarization of syrups in cane mills, Int. Sugar Jnl, 2000, vol.102, No.1223, pp. 568-578.