The Automated Laboratory for Sugar Processing

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ABSTRACT

Sugar is one of the oldest traded commodities in the world. Sugar, coffee, salt, spice, and silk charted trade routes and created intercourse among continents and countries. Economic sources of sucrose are extracted from sugarcane and sugarbeet. The fresh weight of sucrose in these plants can vary from 8 to 22 %, and in the US over 8.1 million metric tons of sugar is produced each year, with 55 % from beets and 45 % from cane for the confectionary, beverage, flavorings, molasses, and pet and livestock markets (1) (2). As a plant, the sugarbeet tends to hold slightly more sugars than sugarcane (ca. 14 -20 % vs 10-15 %, respectively) concentrated in its taproot, and produce different amounts of non-sugars ca. 2.5 % beet vs. 5 % for cane. End products include granulated sugar, gelling sugar, organic sugar, and concentrated juice for food consumption, and pressed and dry chips, beet pulp and molasses for animal feed. Molasses is also a base material in the industrial production of vinegar, citric acid, ethanol, and as a source material in yeast production. In the US, sugar crops are grown, harvested, and processed from cooperative farmers in discrete regions (Figure 1) (3). Sugarbeet is grown in temperate regions, and sugarcane is grown in the humid south. In the last 35 years, smaller family farms have become largely incorporated and harvest larger acreages (4). In the US, sugarbeet farmers owned nearly 40 percent of the total land they operated and rented more than half on a cash-rent basis. Sixty-four percent of US sugarbeet farms had fewer than 250 sugarbeet acres and accounted for only 30 percent of total sugarbeet production, while about 35 percent of the farms with more than 250 acres accounted for 70 percent of the total sugarbeet crop. Combined with labor shortages in rural locations, this has driven automation technologies for planting,

harvesting, extraction, refining, and testing of sugar. This monograph will emphasize automated laboratory testing in the extraction and refining of sugar.

From a global perspective, sugarcane is primarily found in equatorial regions (Figure 2) and comprises 80 % of all sugar production. World sugar trade averages 64 million tons/year. Raw sugar accounts for around 60% of international trade volumes. Although many countries produce sugar, the top five producers (Brazil>India>European Union>China>US) were responsible for nearly 60% of the world production 2020. Brazil, as the largest producing and exporting country in the world, dominates world trade, accounting for about 50% of global exports (5).

The processing for sugarcane and sugarbeet juice has some similarities, and sugarcane mills and their refineries may reside at different locations. As mentioned earlier, each plant contains different amounts of non-sugars, and different content of fiber. The compositional differences require different types of processing and refining (6).

Chemical control in the sugar lab and factory requires support of operators, chemist, IT and chemical engineers. S.J. Osborn recognized this as far back as 1920 (7) as an employee of the Great Western Sugar Company. He stated "In some companies of sufficient size the chemical control work is now handled by a specially organized chemical department, entirely independent of the operating department, although the two naturally enjoy intimate relations and must work in close cooperation to achieve the best results. This system has many advantages. Not only does it relieve the operating department of responsibility for a highly technical line of work, but it puts the results on a basis where they are free from even any suspicion of bias or irregularity and facilitates the introduction and use of uniform methods of analysis and control at all factories of the organization. Naturally it does not pay to develop an elaborate system of chemical control unless the operating and engineering departments are also sufficiently developed to use and apply the data, and the growth of the several departments will therefore go hand in hand."

Automation and control maximize the output and capacity of extracting sugar from plants at the mills and includes the transfer of solids through conveyers, separation gates, slicers, crushers, steamers, and filtering mechanisms. Pulp juice passes through pipes and into filtering/processing/evaporation silos, and centrifuges with control values, motors, drives, mass flow controllers, and chemical and physical sensors. Local programmable logic controllers (PLC's), or more ubiquitously driven distributed control systems (DCS) allow plant operators to regulate and monitor the entire factory from a single control

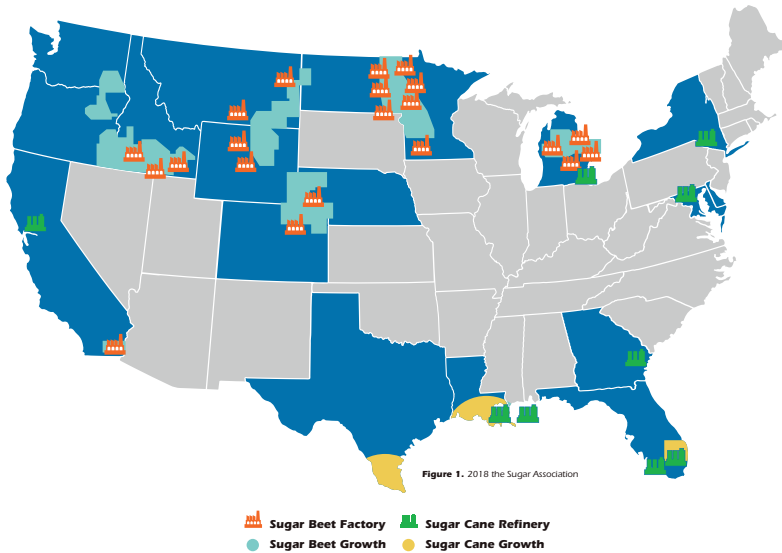**Figure 1.** Sugarbeet and Sugarcane Growth and Factory Locations in the US

Figure 1. 2018 the Sugar Association

Sugar Beet Factory   Sugar Cane Refinery
Sugar Beet Growth   Sugar Cane Growth

Figure 2. World Map of Sugarcane and Sugarbeet Growth

Figure 2.
World Map Ragus

Sugar Cane
Sugar Beets

room. Wired and wireless transmitted chemical and imaging sensors provide feedback to DCS systems throughout the production process. As for the laboratory, data is sometimes transferred to Laboratory Information Management Systems (LIMS) using ethernet protocols. Chemical and physical measurements play an important role in this production, control and monitoring process.

The milling and refining environment requires a combination of in-line, on-line (*inside the pipe or container or bypass, respectively*), at-line (*next to process*), and laboratory analytical measurements at select control points. These chemical analyzers require a team of chemists and engineers to provide simple data logging functions (paper) or more elaborate monitors and controllers using serial (RTU) and Ethernet communications (TCP/IP) via digital analog io using client server architecture and communication protocols (e.g. Modbus, CANbus etc) to DCS, PLC and LIMS systems. Due to ambient environmental conditions, corrosion, temperature, sample build up, sample viscosity, and pipeline cavitation, many chemical sensors are not capable of at-line and in-line/on-line environments. Most samples tend to be tested inside the sugar laboratory under controlled conditions and follow sample treatment guidelines.

Many of the methods for these analyzers have been adopted and validated from the International Commission for Uniform Methods for Sugar Analysis (ICUMSA) (8). ICUMSA is the only international organization concerned solely with analytical methods for the sugar industry and involves 20 member countries. ICUMSA methods are also recognized by authorities such as the Codex Alimentarius Commission, the OIML, the EU, and the US Food Chemicals Codex. The most historically popular chemical analyzer for sugar processing is the polarimeter. In the next section, we will discuss where analytical methods are applied to the sugarbeet process.

The Sugar Beet Process and Control Points

The sugar beet refining process is defined in Figure 3 below and this process has been well documented in several publications (6) (9) (10) (11). Analysis of process steps by sugar factory laboratories generates analytical data for process operators and managers. A common term for this function is Process Quality Control (PQC). Final product analysis, for the various products made by both beet and cane sugar factories, verifies the final product meets quality specifications. A common name for this function is Quality Assurance/ Quality Control (QAQC). PQC is best done in-line or on-line, because data is real time and can be used in process control strategies. For at-line and laboratory, once a sample is obtained, brought to the lab, prepared for analysis, analyzed and reported

the extended time delay is not optimum for process control. However, sometimes a sample must be conditioned before analysis, or the environment is not favorable for sensitive analytical equipment, and in these instances in-line and on-line monitoring are not possible. QAQC is associated with a batch or lot and is best done before shipping, using a positive release type of control for final product shipping approval. Critical control points are pinpointed in the Sugar refining process for monitoring and control. In the next section we review where PQC and QAQC are required at the various sugar refining steps.

Laboratory PQC Review analysis of sugar beet process steps (Figure 3)

Figure 3. The Sugarbeet Manufacturing Process Simplified Version
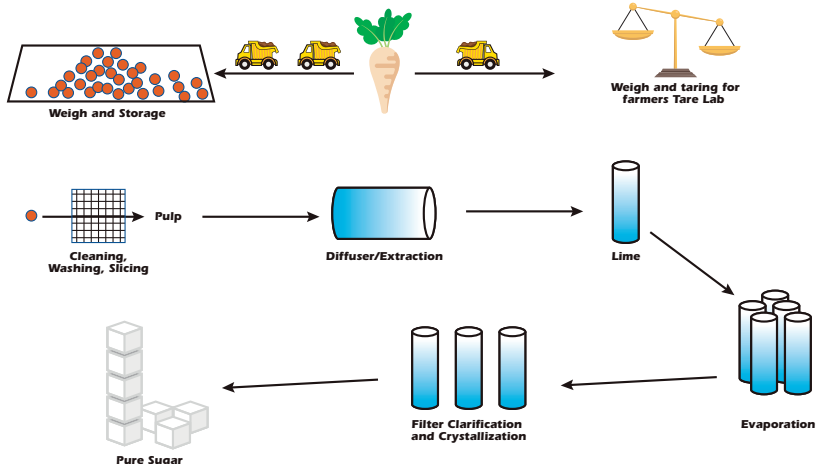
Taring

A special remote laboratory section of the sugar beet facility is normally dedicated in this section, and it is called the tare lab. This section of the process is where sugar content is calculated for royalty payments to farmers, and a small quantity of sugarbeet are obtained from the field to calculate sugar payments. A dedicated section on the tare lab is provided in the last section of this review. Popular analytical tools in the tare lab are the polarimeter, NIR, ion selective electrodes and the conductivity meter.

Pretreatment: Beet fluming, Cleaning, Washing and Slicing

Beet fluming of sugarbeets is the water transport system in the plant, and possible because the sugar beet has a density slightly lower than water. Washing to remove trash and stones along generally occur in the transport system. Slicing of the sugar-beets into cosettes (V-shaped

ribbons) are the initial operations (9) after prolonged storage of the beet root. Sugar beet flume and wash water PQC analyses include similar environmental concerns for water treatment: Total suspended solids (TSS), total dissolved solids (TDS), total organic carbon (TOC), biological oxygen demand (BOD_5), chemical oxygen demand (COD), percent sucrose, glucose, lactic and other organic acids, pH and ammonia.

The main purpose of the slicing operation is to improve the diffusion operations. Visual inspection, weight and length of cosettes are the primary quality indicators in this section. However, cossettes can be a good medium for microbial activity, and they should be monitored for microbial presence.

Diffusion

Once cosettes are washed, the trip to extraction is short. The diffusion or osmosis process begins inside the diffuser with applied heat, and the products are diffusion juice and pulp. PQC analyses include: percent sucrose of beets, pH, purity of sugar beet extract, percent sucrose, purity and dry substance of the extract or raw juice and microbiological markers such as lactic acid and glucose. Beet juice has a pH of 6.0 to 6.5, and the optimum pH of diffusion juice is 5.8 to 6.0 to prevent biological activity and inversion (9). A high temperature (> 70°C) optimizes diffusion rate, promotes denaturization, and minimizes microbial activity; however, it also increases pectin released to the juice, and minimizes pulp pressing ability. Too low of a temperature (<70°C) create optimum conditions for microbial activity with deviating problems of inversion and filtration. The ideal temperature is 70 to 73°C during the diffusion process (9).

Liming and Carbonation

Liming and carbonation are the most complicated and important purification step in the production of sucrose from sugarbeet. Juice purification consists of liming (carbonation lime), carbonation gas (gas), sludge separation and sulfurization. The pH of factory liquors is of considerable important as described above. Laboratory tests have shown that carbonatation is very effective in the removal of a number of impurities such as color, turbidity, starch, gums, magnesium, sulphates, phosphates, magnesium, and removal of floc precursors in the melt; however lactic acid buildup is possible (12) (13) (14).

Below pH 7 sucrose is hydrolyzed to the reducing sugars glucose and fructose, while above pH 9, alkali destruction of sugars occurs, and colored components are formed. At carbonation, most if not all microbiological activity halts due to high temperatures, pH and liming process e.g. at the last stage of carbonation the pH is reduced to about 9. The calcium carbonate removes colorants, coagulates proteins, gums and the high alkalinity destabilizes monosaccharide sugars. The need to measure microbial activity is lost, but the measurement for the destruction of glucose throughout the carbonation process is necessary. Also added to the analysis load are alkalinity, calcium ion (lime salts) and

CaO concentrations, calcium carbonate (lime mud) settling rate and sucrose losses along with pH.

Sulfidation is the last step (15). Sulfur dioxide is added to prevent browning and inversion that can occur at the evaporator and crystallization step, sulfidation prevents the juice from becoming too alkaline, and acts as a biocide. The final product of this process is commonly called thin juice. Here pH, percent sucrose, purity, RDS, density either measured or calculated from dry substance, and calcium ion concentration and color are commonly determined. Most of these analyses are difficult to bring online so samples are drawn and transported to the QC lab.

Evaporation

Multiple effect evaporators concentrate thin juice to a much higher concentration or brix exposing the solution to high heat. If the solution is not stable to pH change, several problems occur affecting purity through the production of non-sugars and color. Density has been put online here with an online density meter. However, sucrose concentration, pH and color are more difficult for online analysis and these samples must be brought into the laboratory for analyses. As example, a critical parameter for measuring the super saturated liquor is the super saturation coefficient K_{SS}. This is a function of dry substance (refractometer) e.g. the larger the dissolved solids the larger the K_{SS} and the higher the sucrose content, purity (polarimeter and refractometer), temperature and saturation coefficient (9).

Multiple filtrations

Filtering small particulates from the various solutions or liquors starts at thin juice and ends at the final feed liquor to the vacuum pans for crystallization. If filter life is poor, operations are very difficult and there is little laboratory analysis can do to find solutions.

Crystallization

A high purity liquor is used at the start of the crystallization series. Crystallization is a two-phase process: nucleation and crystal growth. The liquor/crystal masses are separated with sequentially lower purity liquors used in a series of downstream crystallizations, finally ending up with molasses. Here, the sucrose concentration is low enough standard crystallization is not possible. Purity, dry substance, density either calculated or measured, color and pH are determined for these processes with the added step of diluting the sample for analysis. Online measurement of density is common in vacuum pans to monitor concentration and help control crystallization.

Crystal separation

Crystal separation is performed on industrial centrifuges and requires at least some analysis to monitor the effectiveness of the centrifuge screens. Purity and dry solids of the separated liquors will determine if

there are any holes in the screens. The analysis of the spun off liquors can help determine the effectiveness of many crystal mass/liquor parameters as well.

Crystal drying and cooling

This step focuses on moisture. There are online NIR instruments that under the right conditions work well "ICUMSA procedure"

Crystal Storage and shipping

The final sucrose crystal product is shipped in various sized containers and transported in trucks and rail cars. Each lot code has an analysis linked to it. This typically includes color, sieve analysis, ash, SO_2 and moisture content. A foreign material determination is made also. All these measurements are performed in the sugar lab.

Next, we describe the fundamental principles of each laboratory method, and how they can contribute to each part of this process.

MATERIALS AND METHODS

note below each technology section we describe the equipment, materials and methods utilized in the automation systems in the tare labs (Amalgamated Sugar) and Sugar Laboratory (MinnDak).

Polarimetry

In 1815 polarimetry (oddly enough) established itself on a sugar solution (16) (17) The famous French physicist, Jean-Baptiste Biot, discovered that a solution of sugar possesses a property called "optical activity" or experimentally observed optical rotation signified as α, when a beam of plane-polarized light gradually rotates on its passage through the solution (Figure 4). The angle of rotation is proportional to the distance traveled in the liquid and is approximately proportional to the sugar concentration. From this a quantity called "specific rotary power" or now known as "specific rotation", [α] which is characteristic to that solution. The specific rotation is dependent upon the wavelength of light, with 532 nm or 880 nm commonly used in modern polarimeters for sugar analysis, the optical rotation (α), the temperature of the sample, the pathlength, (L) and concentration (C) (18). Optical activity is observed when molecules are dissolved in a fluid or due to the fluid itself (neat) only if the molecules are one of two (or more) stereoisomers; this is known as an enantiomer.

$$[\alpha]^T_\lambda = \frac{\alpha^T_\lambda}{L \times C}$$

Some substances rotate the light to the right (or clockwise) as viewed looking towards the light source, we assign this rotation (α, or [α]) as (+), and some to the left (or anticlockwise), signing (α, or [α]) as (-). The

Figure 4. Polarimetry and Optical Rotation. *In 1815, Jean-Baptiste Biot, discovered that a solution of sugar possesses a property called "optical activity". Historical configuration at left,   with tungsten bulb (or candle), and the human eye as detector. Modern polarimeter at right with Faraday module and PMT detector.*
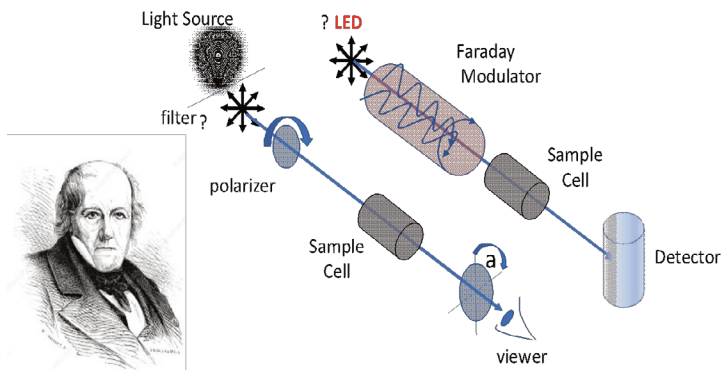

Figure 5. Sucrose Chirality. *Sucrose consists of a glucose unit attached to a fructose unit. Glucose and fructose are regarded as impurities due to the difficulty in crystallizing them from solution. The chiral centers of sucrose are the carbons with up to 9 chiral centers and cannot be represented as a mirror image. Chiral centers in sucrose are carbons 1,2,3,4,5 in glucose, and carbons 2,3,4,5 in fructose. There are up to 16 combinations for stereoisomers for glucose alone! Simple D and L mirror images for glucose are shown for representation.*
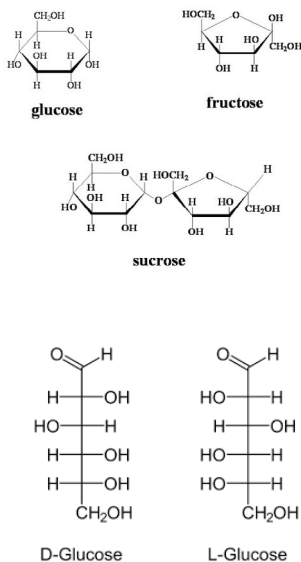
specific rotation of sugars depends on the kind of sugar, and it can be either to the right (dextro-) or the left (laevo-). This has given rise to the name's dextrose and laevulose which were often used for glucose and fructose, respectively (Figure 5), the building blocks of sucrose.

The requirement for a stereoisomer is that the structure of the molecule is not identical to its mirror image and this would exhibit "chirality". Thus, to display optical activity, a fluid must contain only one, or a majority of one, stereoisomer. If two enantiomers are present in equal proportions then their effects cancel out and no optical activity is observed; this is called a "racemic mixture".

Physicist sometimes describes the behavior of light in terms of phase velocity and changes in refractive indices through fluids which can be impeded by these effects, but for a chemist the math is simplified. For a pure substance in solution, if the wavelength and pathlength are fixed and the specific rotation is known, the observed rotation can be used to calculate the concentration. This usage makes a polarimeter invaluable for those trading in or using sugar syrups in bulk (19). In the last 150 years it is hard to attribute increase in sugar yield from beet and cane plants without the use of the polarimeter. The rate of progress was accelerated by using the polarimeter which had already been introduced by Vaentzke for analyzing different kinds of juice, and into beet breeding around 1853 by Vilmorin. 50 years later, S.J. Osborn in *The U.S. Journal of Industrial and Engineering Chemistry* in 1920, declares that without polarimeters "...the sugar industry would still be in the dark ages" (7).

Gone are the days of direct readings in sucrose concentration using wedges and plates from quartz. Modern polarimeters utilize modulators, photomultiplier tubes, Peltier cooling for temperature control of sample and detectors, digital controls and displays for touch screen with graphical user interfaces (GUI's). All of these features can contribute to the high precision +/- 0.001 °α analysis, but a tolerance of +/- 0.01 °α is a satisfying specification for the sugar lab. Thus, temperature control is typically not required in a sugar polarimeter at +/- 0.01 °α, and in most sugar lab environments the samples are moving swiftly through a funnel or flow cell and absolute temperature control slows the pace of analysis. However, the temperature of the solution is measured, and a sugar temperature correction algorithm is employed.

Another modern feature is the Faraday modulator (20). A Faraday rotator is based on the magneto-optic effect which in the interaction of light with the magnetic field in a medium. The Faraday effect causes a rotation of the plane of polarization which is linearly proportional to the component of the magnetic field in the direction of propagation.

Polarimeters are given special attention in this paper because they are omnipresent in the sugar industry and are called saccharimeters because of this popularity. There are over 12 saccharimeter methods developed by ICUMSA for sugar, syrup and molasses analysis (8). Rather than optical rotation (α) or the concentration dependent specific rotation

([α]), the unit the unit expressed by a saccharimeter is °Z. ICUMSA recommends a saccharimeter with an accuracy of +/- 0.01 °Z (ca. 0.03 α). Based on the International Sugar Scale (ISS), a 100 °Z point (or 34.626 ° degree) corresponds to a normal solution of pure sucrose, defined as 26.0160 g of sucrose dissolved in 100 mL of water measured at 200 mm at 20 °C and 589 nm. The ISS is linearly divided, i.e. a rotation of +17.313° (13 g/100 mL) is equivalent to a reading of 50.00 °Z.

Polarimetric methods for the determination of the concentration of sugar contaminants e.g. dextran and raffinose include steps of measurement of the optical rotation of a solution sample, treatment or filter of the sample with a reactive agent, and measurement of the optical rotation of the sample after treatment to ascertain the concentration of impurity.

Dextran is an extracellular bacterial homopolysaccharide of D-glucose composed predominantly of α-1,6-glucopyranosidic linkages within the main chain. Dextran not only causes sugar losses due to dextran formation but dextran itself causes processing problems due to increased juice viscosity (flow issues), poor clarification, and crystal elongations are all associated with the presence of dextran (21). Dextran has potential to form cross linkages that results in the formation of gels (22), which increases viscosity. Dextran contamination in sugars can also cause issues for alcohol beverage manufacturers because it is not soluble in ethanol (23). Dextran in juice, syrup and sugars can cause false polarization. The dextran molecule is highly dextro-rotary having a specific rotation (SR) three times greater than sucrose, this provides misleading SR values for sucrose analysis and overestimation or overpayment to coop farmers (24).

Dextran is formed by decomposition of sucrose by certain lactic acid bacteria of the family *Lactobacillus*. 95% of polysaccharides produced by sugar beet spoilage organisms are homopolysaccharides—dextran or levan (25). Species can include *Leuconostoc mesenteroides* and *Streptococcus mutans* as driving factors. The primary bacterial rot organism was the lactic acid bacterium *Leuconostoc mesenteroides* subsp. *Dextranicum*. *L. mesenteroides* produce dextrans (a- (1 6)-a-D-glucans) and other deterioration products including mannitol and D-lactic acid, which in moderate and severe cases can disrupt sugar processing operations. *Lactobacillus* species also have been found associated with sucrose inversion (26) . While dextran formation is not negligible due to freezing and thawing cycles in stored sugarbeet locations, dextran in sugarcane can be more of an issue, and can cause overpayment of farms for their cane crops (27) due to the polarization issue. Dextran can be formed if the cane stays in the sun for too long before being treated in mills.

Raffinose in an oligosaccharide that causes contamination and leads to over estimation of sucrose concentration (due to higher optical activity), and is more predominate in beet than cane samples. Raffinose levels in initially harvested sugarbeet are low ca. < 0.2 %, and higher raffinose

levels are associated with beets grown in cooler climates, although considerable varietal and seasonal differences are observed. However, Raffinose is a common deterioration product in stored beet (28). Estimation of dextran and raffinose are important parameters to track during sugar refining.

Enzymatic hydrolysis and liquid filtration polarimetric methods have been proposed to replace the more commonly used dextran Haze method which is based upon turbidity (described below). The polarimeter methods have the advantage of being less sensitive to molecular mass as with the Haze method. These methods specify techniques for measuring dextran without the optical activity influence of sucrose.

In addition to polarimetry, ICUMSA recognizes other laboratory technologies such as refractometry, density, chromatography, (HPLC, GC, Ion, etc.), spectroscopy (Raman, UV, color, NIR, MIR and NMR) electrode and optical probe analysis (pH, ion selective, conductivity, turbidity), and isotopic discrimination. All these methods have been used on wide variety of sugar syrups, inverted and non-inverted types.

In the tare lab at Amalgamated Sugar a *Rudolph Research AP880* saccharimeter was utilized for measurements with an accuracy of +/- 0.01 Z. The AP880 comes standard with two wavelengths: 589 nm and 880 nm. Due to the clarity of the solutions, the 880 nm was utilized for all tests. The automatic saccharimeter is an automatic sugar polarimeter, calibrated in °Z of the International Sugar Scale in accordance with the ICUMSA recommendation for 200mm pathlength cell and 26g/100ml normal weight. The AP880 has one RS232 serial port, 2 USB ports, and one ethernet port. The communication with the factory output display was accomplished through RS232, though automated control with the ethernet port is possible. A 41T-8.5-100-10 stainless steel flow through polarimeter pour funnel sample cell with an 8.5mm inside diameter, 100mm optical pathlength, a 10ml volume and a port for a temperature sensor were utilized. Samples were poured directly into a funnel. A multiplier was used to convert the pathlength to 200 mm. After each polarimeter analysis the samples are automatically pumped through tubing to cups for the nitrate ion selective electrode.

The system is validated with *Rudolph Research* right turning quartz plate with an optical rotation approx. +34.000° Arc at 589nm or approx. ±98° ISS (°Z) at 589nm. quartz control plates are manufactured and calibrated by Rudolph Research and are traceable to the National Institute of Standards and Technology (NIST).

In the sugar laboratory at MinnDak a *Rudolph Research an AP880* was also implemented. However, the AP880 was incorporated into the *Rudolph Automation R837 Autoflex.* A 32-5-50-1.0-HP high pressure, stainless steel polarimeter sample cell was utilized with a 5 mm inside diameter, and a 50 mm optical pathlength, a 1 ml volume and a port for the temperature sensor. The 50 mm cell was utilized to allow faster and lower volume cleaning fluids after each analysis.

The Autoflex automation system has a carousal test tube arrangement capable of holding up to 50 test tubes. The tubes 16 mm x 100 mm hold up to 14 ml of liquid. Custom racks can be designed for various container sizes. An automated bar code reader is possible on each tube; however, we utilized the software input for each sample. The tubes are capped with a plastic cap that allows for needle penetration. The sample can be withdrawn using pressure or vacuum mode. We utilized vacuum mode for all tests. At least 10 ml of sample is withdrawn and travels through the pH meter>refractometer>density meter>polarimeter>UV/VIS. We describe the other technologies below. The rinse station resides to the side of the Autoflex, and a rinse step between samples includes water, acetone, and drying. Data communications to the LIMS system for all results goes through the ethernet.

Refractive Index/BRIX/RDS

Refractive index is a basic optical property for a material and determines how much the path of light is bent, or refracted, when entering a material (Figure 6). It is a dimensionless number, which describes how fast light can travel through a medium. It can be used to determine the composition and concentration of a solution. The refractive index varies for concentration, pressure, temperature and wavelength. Most chemists can recite that the refractive index of water is 1.33, while other materials such as diamonds are very high on the scale at 2.42. Very few liquids have a refractive index less than water, nor greater than cinnamon oil ca. 1.6. The sugar industry tends to use RDS and Brix rather than the dimensionless refractive index.

Figure 6. The Modern Digital Refractometer for Liquids. *A liquid is dropped on the prism or passes by the prism in a flow cell. This configuration is similar to an ATR geometry for mid-infrared. The light is reflected and undergoes refraction through the medium. Less than 1 mL of solution is required for analysis. Rudolph Research's "Smart Sampling" can provide the user information that sample is present and the prism is clean.*
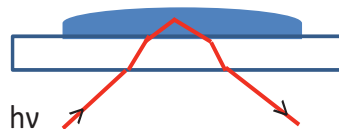
Brix is a measure of the sucrose or sugar content, and can be converted using several optical, physical and spectroscopic methods e.g. refractive index, infrared, density or specific gravity. Second to the polarimeter, it is a very popular measurement in sucrose refining. Adolf Ferdinand Wenceslaus Brix (20 February 1798 – 14 February 1870) was

a German mathematician and engineer. This parameter evolved with other famous names with units named after them, Karl Balling, followed by Adolf Brix, and Fritz Plato. Each successfully created more accurate tables for using specific gravity to Balling/Brix/Plato's, and at the time were more focused on creating a table for a brew master to determine sugar in wort.

We think of the Brix percentage as measure of the sucrose, or sugar content. One-degree Brix is equal to one gram of sucrose in 100 grams of solution. This means a solution that is 20 Brix is equal to 20 % sucrose; assuming that the solution is pure sugar of course. While Brix is more universally determined by refractive index it should be referenced as such. RDS is refractive index dissolved solids, and solutions containing only sugar and water, % RDS = Brix = % sugar by mass. If the solution is just sucrose and water the conversion tables work well; however, there are circumstances when other substances are dissolved in solution with the sucrose. In this case, a unique table to the sample composition is required (in soft drinks for instance), or the Brix value may be used as an indicator of compositional and concentration changes in the solution. Syrup is produced in the evaporation phase with about 65° Brix, and various phases of the process will have BRIX /RDS expected values. As with polarimetry, we will describe ideal control points and automation for refractive index.

In the sugar laboratory at MinnDak a *Rudolph Research J457OM* with 589 nm LED, with a flow through presser was incorporated into the R837 Autoflex station. The system is constructed with a sapphire prism surrounded by a stainless-steel mounting ring. The measurement range is 1.26 to 1.72 refractive index or Brix 0 to 100 %. The accuracy in refractive index is +/- 0.00002 or Brix +/- 0.015. Temperature is controlled by a Peltier at the prism. The Smart Measure modes indicates if there is sample along the sapphire prism (e.g. in the flow cell). Units are measured in refractive index, but converted to Brix and RDS in the Autoflex software package. The system is zeroed with RO water during cleaning cycles. A dodecane refractive index standard at 1.421 is used to validate the refractive index module at it is certified at 15, 20 and 25°C.

Density/Specific Gravity

Hydrometers are still used in the sugar lab, but much greater accuracy and precision is obtained with an electronic oscillating capillary U-Tube. This oscillation frequency is converted to density in which the sugar content is converted to percent by mass (Figure 7).

Density is defined as mass per unit volume. Specific gravity is the density of a material at a certain temperature divided by the density of water at a certain temperature, ca. divide 0.99823 g/cc at 20 °Celsius. As described earlier, specific gravity was the basis of the Balling, Brix and Plato tables. Various tables can be used to convert to °P or °Bx. For ICUMSA sugar is reported in mass fraction m.f. The dissolved sugar content was originally estimated by measurement of specific gravity

Figure 7. Digital Density Meter Principles. *The Density Meter's glass U-tube (the sample cell) acts like a tuning fork. Imagine, that the tuning fork is a capillary tube, and if the tube is filled with water, the tone will become lower and the time required for a cycle of oscillation is now longer. The nature of the frequency or period depends upon the mass and subsequently the density of the materials filling the set volume (~2 mLs) oscillator.*

using a hydrometer or pycnometer, and now largely replaced with the digital density meter.

In the sugar laboratory at MinnDak a Rudolph Research DDM2911 is incorporated into the Autoflex for density measurements. This process controller in this system also serves as the controller and display for the Autoflex. The refractometer module software can also be accessed from this device. Ethernet communications at the back of this device communicate to the LIMS system. The working range for density is 0 to 3 g/cm^3 with an accuracy of +/- 0.00005 gm/cm^3, and a repeatability of +/- 0.00001 g/cm^3. The sample volume inside the glass U-tube capillary is approximately 1 mL. The Video View™ features allows magnification of the u-tube to determine that here is sample in the U-tube and/or bubbles. An automated bubble detection feature times the system out if bubbles are present. The sample arrives from the refractometer and exits the density meter to the polarimeter.

Ion/pH & Conductivity

Ion selective electrodes (ISE) play an important part in sugar refining. There are several types ISE's available. The glass body, solid state, (crystalline membrane), liquid ion exchange (polymer), and gas sensing. The potential of an ISE can only be measured against a suitable reference electrode in contact with the same test solution. The voltage of the glass electrode, relative to some reference value, is sensitive to changes in the activity of certain type of ions. The glass electrode mainly measures single charged ions NH_4^+, Na^+, Ag^+, and pH is a member of this family where hydrogen ions are measured. pH is measured throughout the sugar refining process in-line, on-line and in the laboratory.

Controlling pH and preventing hydrolysis throughout the process is a deterrent for inversion, but there are other reasons for monitoring pH. Liming raises the pH and precipitates dissolved organics. In this process the sugar juice is initially low at around (ca. 4.5–5.5) and initial liming brings the pH up to a neutral pH of 7.0 – 9.0. Eventually, liming increases the pH up to ~ 11.0 which, along with increasing the temperature of the sugarcane juice to above its boiling point and precipitates the dissolved organics.

After raising pH, the sugarcane juice is carbonated (CO_2) to remove the lime. This lowers the pH and Ca is removed, which is a control point to monitor Ca with a Ca^{++} ion selective electrode (see below). Carbon dioxide reacts with the dissolved calcium hydroxide and produces insoluble calcium carbonate and can lower the pH. The extent of carbonation is monitored with pH. Once the pH drops below 9.0, most of the calcium will have precipitated. A final filtration step removes all suspended solids including both precipitated organics and calcium carbonate solids.

Sugarcane juice is returned back to a low pH before concentrating and crystallizing the refined sugar, SO_2 dosing can return the pH to a range of 5.0–6.0, and at the same time, it prevents glucose and fructose molecules from reacting to form colored compounds. It can also act as a biocide to disinfect the juice before the sugar content is high enough to be antimicrobial. A common method of introducing sulfur dioxide is through on-site reaction of sulfur with oxygen since transport of liquefied sulfur dioxide is expensive.

Chloride, nitrate, and calcium ion selective electrodes have been found to be satisfactory for the determination of the corresponding ions in highly refined white sugar, molasses and other impure sugar samples at different stages of sugar manufacturing or refining. However, ISE's for nitrate and calcium require sample preparation and are not conducive for automation and intertwined with other sensors.

Conductivity electrodes measure the composite ion concentration or activity in a solution. A conductive probe can measure TDS, assuming all the dissolved solids are ions. Pure sucrose in solution has no conductivity because sucrose does not dissociate into ions and the result is zero conductivity. Obviously, this assumes the water is completely free of ions. In most cases, a conductivity electrode is sensitive to 1ppm or better.

The simplest kind of conductivity electrode used consists of two similar electrodes, which measures low conductivities; though four and six pole designs are available which eliminate polarity and line cable resistance issues (Figure 8). In a two-pole design, an alternating voltage is applied to one pole and this causes ions in the solution to migrate towards the pole. The more ions in the solution, the greater the current which flows between the conductivity electrode's poles. The unit of conductivity is S/m or S/cm. The scale for aqueous solutions begins with pure water at a conductivity of 0.05 uS/cm at 25 °C. Naturally occurring

Figure 8. Conductivity Electrode Designs. A four pole with 6 electrodes shown below.

waters such as drinking water or surface water have a conductivity in the range 100 - 1000 uS/cm. Conductivity measurement can validate the purity of the mixed feed syrup in crystallization chambers and monitor ion exchangers used in the refinery. For sugar cane refiners, conductivity is an indication of the ash contained in a sample. Because of the size of pH probes and ion selective probes, they are easily incorporated into laboratory and at-line automation systems.

In the sugar laboratory at MinnDak a Metrohm 780 pH meter was incorporated into the Rudolph Research R837 Autoflex system with a Rudolph Research pH flow cell. The pH working range is 0 to 14 with a resolution of +/- 0.001.

Absorption, Emission and Scattering Spectroscopy

Several fundamental light properties occur in liquids in the UV-MIR region of the electromagnetic spectrum (Figure 9), and boundaries between these regions are not rigidly defined. The regions are partitioned by the wavelength of light, or a phenomenon that occurs in a region(s). For example, fluorescence, Raman and turbidity are optical phenomena's that occur from the UV -> NIR.

UV/VIS Absorption Spectra or Color: The unifying feature of ultraviolet and visible region is that *absorption* in this region causes excitation of electrons to higher energy levels (Figure 10). This transition provides information on the structure of the molecule, and depending where it occurs, can determine other molecular properties such as color. The phenomenon of color can be described mathematically and absolutely, or it can be described what we as humans observe with our eyes, which is generally referred to as the visible region from 380 to 780 nm and goes from violet/blue/green/yellow/orange/red. Chemical analysis methods may use a colorimeter, or a UV/VIS spectrophotometer. Despite the name of the analyzer, it is not uncommon to select wavelength or wavelength region for UV/VIS absorption for chemical analysis. It is best to describe sugar and impurities into groups based upon these measurements.

For UV/VIS spectroscopy and based upon Beer-Lambert law the high absorption peak of sucrose solution is at 197 nm associated with sigma and phi* electronic transition of carbon in the sucrose molecule. However, several other regions are utilized to seek out impurities in sugar.

Figure 9. Electromagnetic Spectrum and ICUMSA 420 for calculation of color for sugar. *The electromagnetic spectrum displays working regions for many optical technologies e.g. color scales, UV/VIS absorption, Fluorescence, Raman, near-infrared, and infrared. There are numerous scales for color, but ICUMSA 420 recommends measuring absorption at 420 nm and dividing by the b=pathlength, RDS from a refractometer, and the density. The density can be mathematically calculated from the RDS or refractometer, or more accurately measured directly from a density meter.*
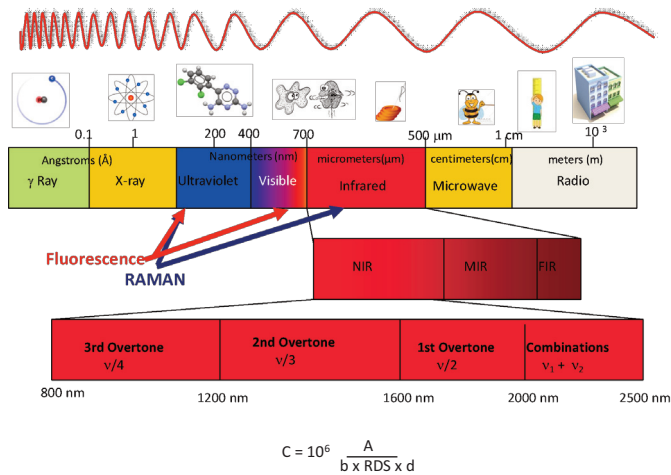

$$C = 10^6 \frac{A}{b \times RDS \times d}$$

Figure 10. *Jablonski diagram and spectra. In molecular spectroscopy, a Jablonski diagram is a diagram that illustrates the electronic states of a molecule and the transitions between them. Spectra at right*
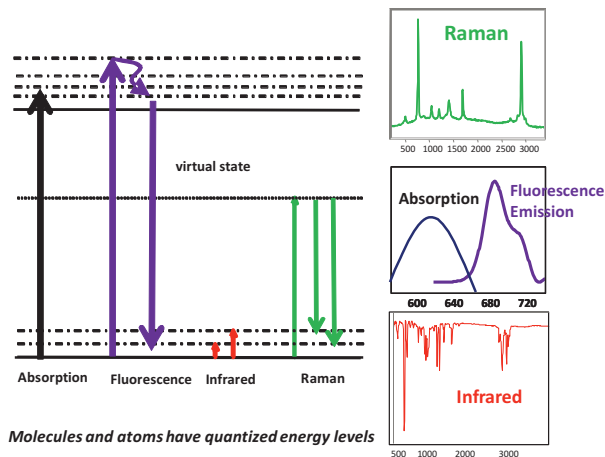
Figure 9 describes a method universally accepted for color of sugar at 420 nm (ICUMSA 420 color) (8), which is in the violet region. It should be noted that both ash and dextran are essential components of molasses, a side product of sugar refinement giving brown sugar its distinct color. U.S. (29) and European pharmacopeias require a color test and UV absorbance data at 420 nm to specifically test pharmaceutical-grade sucrose for molasses remains.

Emission Spectra (Fluorescence): Delayed reemissions at longer wavelengths than the absorbed radiation is an emission event and has been described as luminescence e.g. fluorescence and phosphorescence (Figure 9). In fluorescence the delay is shorter and a more common spectroscopic method. Rigidity of the molecule usually plays a part in its luminescence capability, and although few compounds exhibit luminescence, a few important substances of biological, pharmacological, and organic nature exhibit luminescence behavior. When a fluorescent event occurs, it is typically highly sensitive and selective. Sucrose does not exhibit fluorescence activity, but impurities in solution with sucrose can exhibit high fluorescence.

Fluorescence is more important to detect sucrose impurities. Various amounts of fluorescent impurities of different compositions have been found in various sugar products. The fluorescence spectra are attributed to combination of various fluorophores, two of which have close similarities with tryptophan and tyrosine and could be responsible for the fluorescence pattern one at ca. 280/390 nm. Other fluorophores have been identified as catechol formed by base-catalyzed sugar degradation and again other are suggested being Maillard reaction polymers. These tests are more commonly used for pharmaceutical excipient testing.

Raman Spectroscopy: Raman spectroscopy is a scattering phenomenon and a form of vibrational spectroscopy that can occur from the UV to the NIR. When monochromatic light encounters matter, there is a small probability it will be scattered at the same frequency. If the object is smaller than the wavelength of light it is Rayleigh scattering. If the electron cloud of the molecule is perturbed by molecular vibrations (polarization), and it is possible for optical and vibrational oscillations to interact, this leads to Raman Scattering. Polarizability is ease of distortion of a chemical bond or electronic cloud. The "virtual state" is not necessarily a true quantum state of the molecule but considered a very short-lived distortion of the electron cloud caused by the oscillating electric field of the light (Figure 9). Fluorescence is the nemesis of Raman scattering and can overwhelm the Raman signal. This can come from impurities or the molecule itself, but it can be countered by measuring at higher wavelengths.

Like NIR, Raman has the advantage to see through glass vials and inexpensive fiber optics and probes can be utilized in reactors and vessels. Most sugar studies published in the literature involve applications of NIR spectroscopy primarily due to the simplicity of the instrumentation

involved (30), and NIR trends to improved concentration measurements because it is not dependent upon a fluctuating laser source in Raman (31) . Mid-IR (MIR) and Raman spectroscopy applications have begun to gain prominence with the advent of improved optics and smaller, more powerful lasers and detectors. Like fluorescence, Raman spectroscopy is not widely used in sugar processing, but it has been demonstrated to measure sugar content in honey, sodas and carbonated drinks.

Turbidity: The second fundamental scattering property measured in UV/VIS/NIR region is *turbidity* and it describes the haze or cloudiness of the solution. Turbidimetry and nephelometry are techniques to measure the scattering of suspended particles in solution. In turbidimetry the source radiation is passed directly through the sample solution (best for high concentrations of suspended particles) and a decrease in light intensity is measured. In nephelometry, the beam of radiation is measured 90° to the incident beam (best for low concentrations of suspended particles). Today, the term turbidity probe is more widely used to describe a nephelometry configuration. The higher the suspended solids count, the more hazy or cloudy the solution. The units are generally expressed as NTU (Nephelometric Turbidity Units) for white light analysis. The ideal NTU of drinking water is 0.1 NTU. White light can be used as a source, but many probes utilize special NIR LED light sources. FNU is best used when the data is measured using an 860 nm light (near IR) with a 90-degree detection angle (ISO7027 compliant). The criterion for scattering is that if the suspended solids have a dimension less that the wavelength of the incident light it is a scattering event, and more representative of the turbidity of the solution, thus the origin for LED NIR sources.

The presence of suspended particles impacts the efficiency the sugar refining process. Suspended particles are removed during clarification. In clarification, a combination of lime, activated carbon, and a clarifying agent can be added to sugar juice to reduce turbidity. Turbidity of the solution is also an indication for filter breakthrough.

Dextran is one of the most popular turbidity measurements at 720 nm. The Haze Method is currently the most used method for dextran analysis in the sugar industry (21) . It based on alcoholic precipitation and measures the resulting turbidity photometrically.

The Haze Method according to the ICUMSA GS1/2/9-15 (2011) measures 15 g/100 g sucrose solutions, which represents thin juices. There is potential for automating this measurement, but it requires several manual sample steps prior to analysis of final solution. The procedure includes the removal of starch (enzymatic decomposition with amylase) and proteins (precipitation with 10 g/100 g trichloracetic acid solution) followed by filtration using filter aid (acid washed kieselguhr) and filtering. Dextran is precipitated with ethanol and the resulting turbidity is measured in a spectrophotometer at 720 nm after 20 min ± 10 s.

MIR and NIR: Comparable to Raman, MIR and NIR are forms of vibrational spectroscopy. The difference is that rather than a change in polarizability for a molecule to become Raman active, it must have a change in the dipole moment for infrared absorption. MIR has very sharp absorption spectra which lends itself to high selectivity e.g. like Raman, but sampling is not as simple as Raman or NIR, and it is more sensitive to water absorption. NIR has broader bands, which corresponds to the wavelength range of 700 to 2500 nm with less selectivity than MIR or Raman, but it transmits through glass vials and inexpensive fiber optics without glass interference, like Raman. Most absorbance for NIR occurs as overtones of localized vibrational modes such as hydrogen bond stretching. Due to the overlap and lack of identification of unique bands, NIR is considered a secondary method and requires more intense chemometric modeling for analysis. Because automation systems necessitate specific mechanical configurations and glass containers, NIR and Raman offer the most opportunistic spectroscopic methods for automation in the sugar lab.

NIR has been implemented in tare labs (32). The NIR is a secondary method, and its data can be derived form a polarimeter, refractometer and a conductivity meter. Rather than make measurement on liquids, NIR employs non-contact diffuse reflectance light scattering to measure Pol and ionic strength in sugarbeet and sugarcane brei. Because of the minimal spot size ca. ~ 1mm and sample blend homogeneity, the sample is typical spun under the NIR light source to fully represent the test sample. While mono-atomic ions, such as Na+, are not molecules and they do not have molecular absorption, their concentrations will influence the water band that is prominent in the NIR. These are usually wavelength shifts that are modeled in the water combination and overtone bands. For pol results, sucrose absorption is heavily weighted in the model. Master calibrations representing more than 11,000 samples have been employed (33) , and then local samples are pulled from the production area and analyzed from the polarimeter and conductivity meter and this data is inserted in the training set, and the new model represents the local production.

In the sugar laboratory at MinnDak a Genesys 50 UV-Vis Spectrophotometer is used to make color measurement at 420 nm. The absorbance value at 420 nm, RDS (refractometer, and the density value are implemented to calculate the colorific value of the solution. A 1 cm pathlength flow cell cuvette is incorporated into the spectrophotometer.

Chromatography

Chromatography systems are automated by the manufacturer, and not incorporated into the daisy chain on instruments described above. There are sample trays designed for various tube sizes, caps and seals. Some trays can hold hundreds of samples. While chromatography is one of the most prevalent tools utilized by the sugar chemist, it does take specialized training and the consumables (e.g. columns and solvents) are costly.

High performance liquid chromatography (HPLC) utilizes sample injectors, tubing and pumps to pass a pressurized liquid solvent ("mobile phase") containing the sample mixture through a column filled with a solid adsorbent material ("stationary phase"). This process separates individual molecules in a solution based on the relative affinities in a liquid mobile phase and stationary phase. There are numerous modes of HPLC (i.e. reversed-phase, normal-phase, ion exchange) that are commonly classified according to the mechanism by which separation occurs. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out of the column, and pass onto a spectroscopic or electrochemical detector. Common detectors are refractive index, UV, conductivity, and amperometric.

Gas chromatography substitutes the liquid mobile phase for a gas mobile phase, and this is also an option for detection of sugars, but the caveat is that the sugars must be volatile. This requires an extra derivatization step, and these lengthy preparation steps has limited its use in the sugar lab.

There are over 6 ICUMSA methods for chromatography, and the most popular is high performance anion exchange chromatography (HPAEC) (8) . The HPAEC method for analysis of sucrose, glucose and fructose in beet and cane molasses was given first action by AOAC International (34). HPAEC has been used to determine the concentration of sucrose, glucose, fructose, (35) raffinose (36), and betaine in syrups and molasses. Raffinose has been shown to occur as a byproduct in beet sugar vs. cane sugar when measuring low concentrations. Other components measured throughout the sugar refining process are lactic acid to determine sucrose losses, acetic acid to determine corrosion issues, and inversion/monosarcharide losses. The five major oligosaccharides have also been analyzed by HPAEC, e.g. 1-kestose, neo-kestose, theanderose, erlose and raffinose.

Polysaccharides are long chain polymers of monosaccharides. Dextran and sarkaran are polysaccharide reported in both stale and stand over cane. Typical problems reported with processing stand over cane include very high syrup viscosities and poor crystallization rates. Each of these polysaccharides have been analyzed in sugarcane products ranging from sugar juices to molasses and high pol brown and refined sugars with HPLC. A combination of enzymic hydrolysis followed by HPAEC separation and detection has been used to determine the polysaccharides and study the seasonal and geographic differences in these polysaccharides. However, the Haze Turbidity method as described above is today the accepted ICUMSA method.

RESULTS AND DISCUSSION:
Control Points and Automation

Automation in tare labs/Payment Points

Sugarbeet companies pay their growers based on beet quality and sugar content, and the tare lab deserves a special section on PQC. This section was briefly described above in the extraction section. The desired sugarbeet for processing has the highest possible sucrose content with low impurities allowing the factory to extract sucrose with the least expense possible.

At harvest, the grower delivers sugarbeet to receiving stations where the beets are off-loaded onto a piler. As the truck is unloaded onto the piler, the sugarbeet are cleaned to remove soil and stacked in carefully constructed piles and stored for the winter. On the piler, between the cleaning and stacking of beets, a sample of 20 to 25 pounds of beets is taken from the load, then placed in a sample bag, which is tagged and sealed for delivery to the Beet Quality Lab (BQL). At the BQL the samples are analyzed for quality.

The quality attributes analyzed at the lab are the amount of tare (dirt, tops, rock left in the sample delivered), sucrose, nitrogen, and salts in the roots. An increase of all but sucrose leads to added costs of extracting the sucrose in the factory.

During the busiest time of harvest, which covers most of October, several thousand samples per day are analyzed. Process automation intertwined with at-line analytical tools is essential for quickly and accurately processing large numbers of samples. Each step a sample goes through is synchronized by a computer program. As a sample is first weighed it is assigned a serial number that will be tracked throughout the lab analysis. Computer programs are written for the PLC to control the system movement based on a timed sequence. At each station, there are Graphical User Interfaces (GUI's) and proximity switches, and their displays notify when certain steps of the process are complete.

Each sample bag consists of 7 to 12 beets depending on the beet size. The sample bags are individually hung upside down onto a hook where they are conveyed to a point where they are individually emptied onto a scale to get a gross or "dirty" weight. Beets are then washed in an enclosed rotating drum to get adhering soil off, dried and weighed again to get a light "clean" weight (Figure 11). The difference in the weights is the tare "net" weight which is converted to a percent and is used to subtract from the first net weight of the beets delivered.

The sample of cleaned beets is then dropped onto a gang of saw blades with the resulting "saw dust", called brei (mashed potato type of consistency) is thrown onto a belt. The remaining slabs of beets are conveyed out of the building to be processed in the main factory. The brei is scraped off the belt and prepared for a series of quality analysis measurements after being weighed and blended with reverse osmosis (RO) water in a sample cup.

Figure 11. Washing and Drying in a Taring Facility. After the sugar beet samples are weighed, they are dropped into a drum (below) where they are washed and dried.

Figure 12. The Automated Lab in a Taring Facility. Pictured is a carousel where the beet brei is weighed, mixed and filtered. Conductivity is taken before filtration and the sucrose (polarimeter) and nitrate is measured after filtration.

The first quality parameter analyzed is conductivity which measures the amount of salts in the sugarbeet. A conductivity probe is inserted into the solution of brei and water to measure conductivity that flows through the solution. There is an inverse relationship between salt content and sugarbeet quality. The higher the dissolved salt content the lower the sugarbeet quality. A higher salt content means higher impurities and more caustic soda is needed to aid processing in the factory. The amount of fertilizer applied, which consists of salts, will aid in lowering or increasing the salt content in the sugarbeet. Field selection and variety can aid in controlling salt content as well.

The brei mixture is then filtered to remove impurities such as pectin's that would further impact quality analysis. The filtrate is analyzed by a polarimeter to measure the percent sucrose content in the sample. After the sample passes through the polarimeter it enters a cup where a nitrate sensor is placed to determine the quantity of nitrate in the sample.

The four quality parameters: tare, sucrose content, nitrate content and conductivity are then used in formulas to determine the sugarbeet quality for each grower.

### Automation in the QC sugar lab.

Years ago, polarimeters and refractometers consisted of a light bulb, knob and some optical readout on a mechanical scale. On higher end instruments, a vernier scale was used. Most of the maintenance and troubleshooting involved seeing no light in the optical readout and then changing a light bulb. pH meters had a pH electrode, two knobs for calibration and a needle readout on a pH scale. To minimize parallax, most models had a mirror behind the needle to avoid getting a different reading depending on which angle you viewed the dial. The pH meter problems were minimal, electrodes were cleaned or replaced as they are now. Similarly, spectrophotometers had a light bulb and a needle readout on a transmittance or absorbance scale. The data transfer was all done with human wetware, paper and pencil. Lab technicians would manually prepare the samples, introduce them to individual instruments, record the readings, look up conversions in a table, calculate the results with a manual calculator and finally record the results by writing them in one centralized location in the factory. The late-night calls to lab managers were primarily about someone not showing up for work which was rare.

Then the instruments switched to digital readouts, knobs and needles were gone. Laboratory instrumentation came with communication ports on the back side that interfaced with data historians on computer servers and the results were automatically tabulated in spreadsheets, LIMS, or digitally communicated to control rooms and fed into PLC and DCS systems. The simplification of this process, from a lab technician perspective, added tremendous complexity for the generation and transmission of results for Information Technology Departments. It created a strong dependency on IT infrastructure to get results calculated from raw data, stored, displayed, and reported.

Now we are seeing a trend where the same sample can be analyzed by numerous instruments, from the same or different manufacturers in a daisy chain configuration. The Rudolph Autoflex system is built to perform the following tests (Figure 13): refractive index, density, $Z°$ by polarimetry, absorption at 420 nm through a spectrophotometer and pH. This system comes with a carousel auto sampler with a range of sample tube sizes options. Operationally, the system is cleaned and dried between each sample. Cleaning consists of water and acetone rinses and forced air-drying cycles. Tubing size and cell volumes are minimized with emphasis on laminar flow throughout the system to save on cleaning fluids and promote fast washout. Cleaning and drying the system between samples eliminates the possibility of sample to sample cross contamination but the shortcoming of a cleaning cycle is longer turnaround times. The layout of the instruments saves bench space as they can be stacked tightly.

Shown in the picture below are a: polarimeter, refractometer, pH meter and probe, density meter, auto sampler, spectrophotometer, cleaning system and an air drier plus some bench space under the polarimeter.

Figure 13. Automation in the Sugar Lab. *Rudolph Autoflex with carousal and test tubes. Fluids moved through the density meter, refractometer, pH meter, polarimeter and UV/VIS Spectrometer. System 1 of 2.*
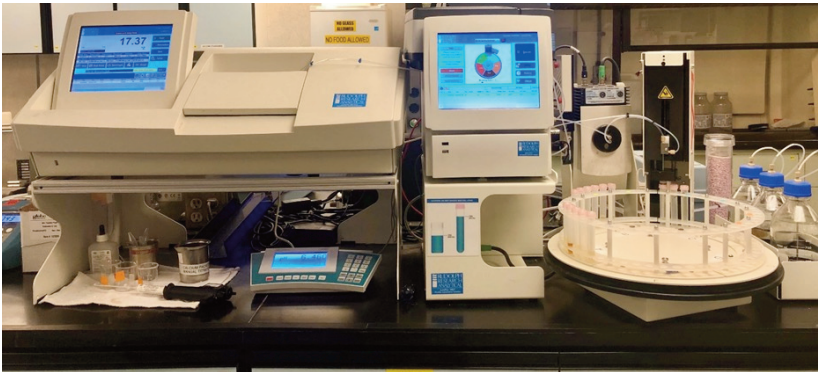
Sample loading options consist of individually labeled sample tubes with bar code identifiers or sample templates. Templates are best for routine hourly analysis. The beet sugar lab has a prescribed schedule of samples each hour and each hour can have its own template. A lab tech would load the template and sequence the correct sample in each slot of the rack. Once all that is done, press the start button and all samples will be processed automatically. If there is a special sample that needs

immediate analysis it can be assigned a high priority and it will be the next in line for analysis. After it is done, the rest of the samples will be processed in their original order. Most of the time, the lab tech only needs to interface with the sample template and be able to put high priority samples into the schedule. If software or connectivity issues arise, teaching them to cycle power may solve those problems without other technical support.

The cycle time is dependent on sample clarity and turbidity. An 8 ml aliquot of clear sample will run in 4.5 – 5.0 minutes through the 5 instruments with the order of refractive index, density, polarimetry, color through spectroscopy and pH. The bulk of the samples run in a beet sugar process lab will be about 5 minutes. However, very dark or turbid samples can time out. Normally it is because of their opacity seen in optical transmission e.g. UV/Vis and polarimetry. Some dark but readable samples will take about 8 minutes to meet the recommended drift requirements or just time out and supply no answer due to sample clarity problems. When complete, data is collected in a report after each run. A reference water sample is used to tare or zero each system as necessary.

To test the linearity and reproducibility, we ran a series of prepared sugar solutions through the 2 separate Autoflex systems. The x-scale on each plot is the sugar samples prepared on w/w basis. Density (g/cc) is the mass of sugar per unit volume and is always slightly less than specific gravity as shown. Specific gravity is the density with respect to reference standard water at 20 °C. This data is obtained from the DDM2910 density meter (Figure 14). The difference between the two measurements are reported statistically as the standard deviation of differences (SDD) across the range of 1.25 and 25 g sucrose/100 g of sugar solution. The percent error is calculated as the standard deviation divided by the average value. These values are significant to the precision/ reproducibility of two independent density meters as part of two separate Automation systems, which is similar to reporting results (reproducibility) in a collaborative study.

The refractometer measures refractive index and it has a direct relationship to sugar concentration. This is referred to as refractometer dry substance or RDS and it is synonymous with Brix for pure sucrose solution. The RDS and the °Z value from the polarimeter can eliminate any non-optically active dry solids from the value, and this provides for a sugar purity calculation. These are weight/weight dilutions prepared from MinnDak sugar standards. Note that the measured BRIX and RDS values are very similar and typically vary by less than 0.01 units because these are very pure solutions. Like the density meter, the refractive index measurement is very linear and reproducible from system to system (Figure 15).

The polarimeter calculates °Z from the optical rotation. The °Z scale determines the concentration of sucrose based on a weight/volume dilution. The rotation of 34.626° corresponds to a concentration of 26 g

Figure 14. Density and Specific Gravity vs Sugar Concentration. *Each datapoint is an average value from the two density meters on two separate Autoflex Systems. Samples were prepared from dilutions.*
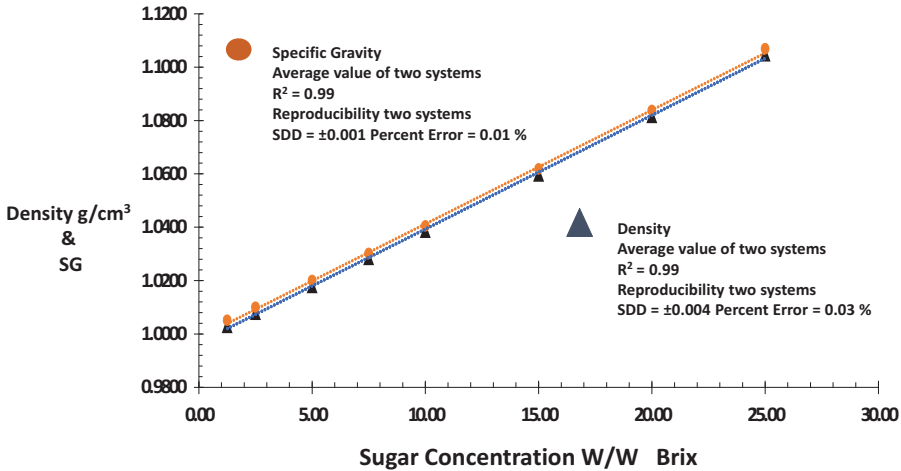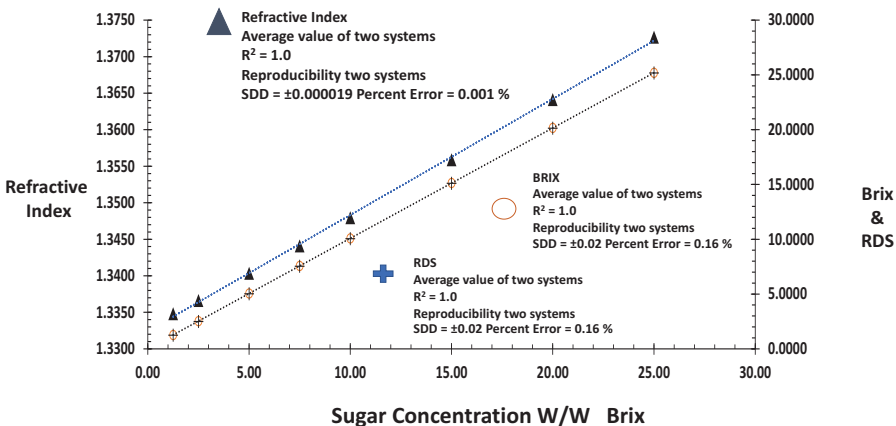

Figure 15. Refractive Index, Brix and RDS. *Each datapoint is an average value from the two refractometers on two separate Autoflex Systems. Refractive Index on Y-axis right and Brix and RDS on Y-axis left. on the Samples were prepared from dilutions. Refractive Index is the principle measurement and then converted to BRIX and RDS.*

sucrose or 100.00 °Z (sucrose) in a 100 mL solution, at 20.0 °C, and at the wavelength of 589.44 nm in a 200 mm sample tube.

In Figure 16, we plot the °Z /density vs the weight/weight-based concentration of sucrose solutions measured. The division by density of a weight/volume sucrose solution will convert that to the weight/weight equivalent for polarimetric determination of °Z or POL of the solution. Note that at 25 % sugar or BRIX we are very near the expected 96.1 °Z mark.

Color and pH are measured in process samples; however, these are clear solution standards with negligible absorption and pH variation. The purity and sugar concentration are automatically calculated in the reports. Purity is calculated from the refractometer and saccharimeter e.g. see ICUMSA Methods Book, Method GS 5/7-1(1994)) by the formula Purity=100(0.26) (°Z-°Z of water prior to measurement)/solution concentration (below). The solution concentration was calculated from the refractometer and density meter where Solution concentration = (BRIX -BRIX of water prior to measurement) (specific gravity).

Figure 16. Degree Z from the Saccharimeter and Density Meter Correction. *Each datapoint is an average value from the two polarimeters and two density meters on two separate Autoflex Systems. Samples were prepared from dilutions.*
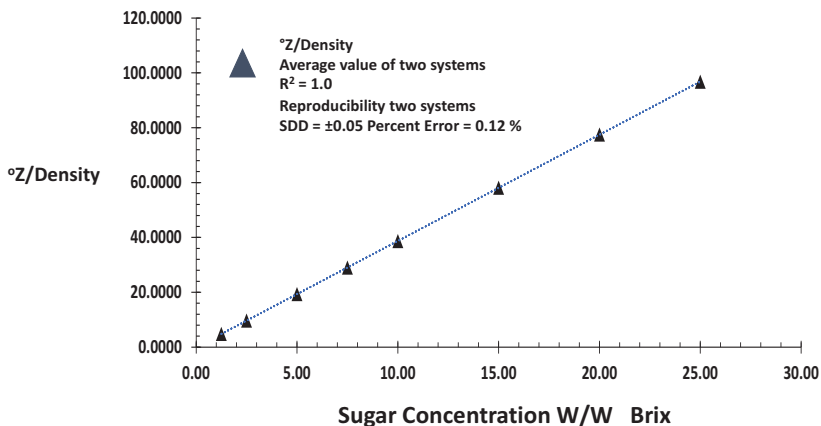
CONCLUSIONS

To echo S.J. Osborn from 1920 (7), chemical control requires cooperation among numerous departments, and automation in the sugar lab and factory require support of operators, chemist, IT and chemical engineers. Process, at-line and laboratory tests are conducted at every stage of the production process for purposes of process follow-up and quality control. Control points that are prohibited from direct sensor control due to sample preparation, remoteness, or mechanical access can also benefit from automation.

The tare lab at Amalgamated Sugar is a prime example where sample preparation is automated prior to testing by the conductivity, polarimeter and nitrate electrode. The beets are processed in pilot operations for tare lab purposes. Each step is automated and the farmers beets are tracked throughout the process for payment. This automation system has been employed for over several years and continues to save the plant in QC costs with savings going back to the cooperative.

Prior to a commercial system, the Minn-Dak automation systems was an in-house designed automation system. In 2018 Minn-Dak upgraded to a commercially available system from Rudolph Research which was the first commercial AutoFlex system in a in a beet sugar factory; however, due to numerous moving parts there were a few startup issues. After these startup issues were resolved, downtime consisted of primarily continued debugging of communication issues between the instruments and the supervisory control PC, networking, operator errors, sample cap alignment problems, changes in tube cap thickness from various suppliers and random-unknown items that required a reboot of the system. In the current system with the software upgrades, general exterior cleaning and zeroing the instruments is part of the operational routine and very little downtime has been experienced.

The return on investment requires a lot of up front work and depends upon the following variables (Table 1).

Payback estimations need to take all these things into account: The value of information accessibility offers a current process snapshot and access to historical trends. Cost of IT resources should be considered as well.

This facility has noticed that when laboratory temperatures reach 90°F, the instruments struggle because some portions support thermoelectric cooling, and it makes it difficult for the heat to dissipate. Ambient dust levels are common in a beet sugar factory and vent filters have to be cleaned accordingly as they plug up. Ambient air maybe a problem if trace SO_2 levels get high enough to corrode electrical connections.

Current lab and process user experiences are positive. The biggest complaint is the turnaround time on the analysis because of the large number of instruments involved and sample to sample cleaning.

Ultimately, the more accurate and timelier the results are the greater

the confidence the plant operations have and the faster they will respond to change in the process. The AutoFlex system performs well and satisfies this requirement.

Table 1. List of variables to consider payback on automation systems

PROPERTY	RUDOLPH 785 AUTOFLEX	CIRCA 1985
LABOR	Fewer lab techs, data streamlined	2 to 3 times more lab techs on similar sample tests, data manually written
TRAINING	Less training but more sophisticated training and requires IT	Training time is longer because of multiple instruments and sampling preparations.
TROUBLESHOOTING	Instrument alarms indicate issues with system.	Instrument diagnostics are manual and step by step troubleshooting.
REPORTS	Math is pre-programed, automated output, numerous, and can travel over ethernet to LIMS.	Require paper, lab and log book inputs, manual calculations and interpretation errors.
SUPPORT AND MAINTENANCE	Require more support for programing and IT, vendors can log in	Phone support only from vendor. Cleaning cells is more time consuming than automation.
SAMPLES	Similar sample preparation, but less sample required. Less than 15 ml of sample required.	More mistakes with manual sample handling, and cleaning cells.
TIME	Less than 10 minutes for 5 instruments for results.	For all 5 separate instruments the time is over 15 minutes, not including cell cleaning and manual calculations.

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