

A NEW POLARIMETER APPLIED TO SUGAR INDUSTRY IN BRAZIL

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Résumé

La croissance rapide de la modernisation de l'industrie brésilienne de la canne à sucre, due à la compétitivité du marché international, a établi le besoin d'utilisation et de l'application des méthodes internationales reconnues pour l'analyse du sucre. Le prix du sucre et des dérivés de la canne à sucre est défini par la qualité du produit, évalué par différents paramètres. L'un des plus importants est la concentration de la saccharose, mesurée à l'aide de saccharimètres. Nous rapportons ici les premières étapes de la construction d'un polarimètre qui servira à l'étalonnage des plaques de quartz étalons pour la vérification des saccharimètres commerciaux.

Abstract

The fast growing modernization of the Brazilian sugar cane industry based on the very competitive international market have set the necessity of adoption of recognized international methods for sugar analysis. The price of sugarcane, sugar and byproducts is set by its quality, evaluated by several parameters, being the most relevant the sucrose content in sugarcane and sugar, measured with saccharimeters. We report in this paper the first steps of the construction of a polarimeter for calibration of quartz control plates, the transfer standards for industry saccharimeter verification.

Introduction

Brazil is the largest sugar cane producer in the world. The impact of sugarcane, sugar and byproducts exportations on Brazilian economy is recognized as a strategic issue. For example the Kyoto Protocol is playing an important role on launching the alcohol as a viable clean fuel, and this will boost the production of ethanol beyond the internal market destination. Trade and business mean technical barriers, regulations and specially, quality control. Some of the sugar and alcohol sectors in Brazil are nowadays well organized, and modern technology is in use and being widespread. They are adopting recognized international methods for sugar analysis, recommended by ICUMSA (International Commission for Uniform Methods of Sugar Analysis) and the OIML (Organization Internationale de Métrologie Légale), in order to standardize procedures in the laboratories at the sugar/alcohol plants. In fact, the quality of the sugar determines the price paid to the cane growers, and also the price paid by the buyers for the exported cane

products. Sugar is a commodity and thus the conformity to international norms and regulations will give a strong backup for Brazil fight in a very competitive international market. In Brazil, the Inmetro—National Institute of Metrology, Standardization and Industrial Quality—is the institution responsible for accreditation and standardization for both legal and metrological aspects, what makes it an important player at this scenario.

The prices of the sugarcane ton, sugar and byproducts are stated by an index from the market and by its quality, entering a formula for price formation. The most important factor is the percentage of sucrose measured in a sugar scale as polarization rotation, called POL by the sugar industry. This scale, defined by ICUMSA conventions, is called the “International Sugar Scale” and the unit is the °Z (from the German word “Zucker”). The polarization rotation of sucrose-containing solutions is determined with an instrument called saccharimeter, a particular case of a polarimeter. Every sugarcane industry has at least two saccharimeters, one for the sugarcane quality laboratory and the other for the industry laboratory to control process and the quality of sugar produced.

The sugarcane is sampled and its juice is tested in order to measure its polarization rotation, among other tests, defining its quality and consequently defining the final price. This is a very sensitive point, where disagreements between sugarcane growers and industry can occur. That is the reason why the OIML recommends periodic verification of the calibration of the saccharimeters by the use of reference quartz plates as transfer standards. These standards need themselves to be calibrated by an accredited laboratory or accreditation body, to ensure traceability. Such service is presently realized at the Physikalisch-Technische Bundesanstalt—PTB, in Germany. The modernization of the Brazilian sugar plants, with the fast growing number of polarimeters in use, has increased the demand for quartz plates calibrations, claiming for a local service in Brazil.

The Optical Metrology Division of Inmetro (Diopt) is now setting up a homemade polarimeter for calibration of quartz transfer standards for the verification of the industry saccharimeters.

The control procedures of the verification of the instruments are fixed in accordance with the national regulations of each country. Inmetro, as an Officially authorized metrology institute in Brazil and member of the OIML, is developing such regulations.

Here we remind the ICUMSA and the OIML recommendations for sugar polarimetry, showing the equations used in the calculations of the related parameters. We report too the first efforts for the construction of a reference polarimeter at Inmetro, and our future project.

The polarimetry methods

The analytical methods for the sugar industry are uniformized under a global association of more than thirty countries: the ICUMSA. The methods are based on the activities of the National Committees for Sugar Analysis of the member countries, and are recognized by authorities such as the OIML. ICUMSA sets the standards and specifications for the international sugar scale to determine the sugar content of sucrose-containing products by the use of polarimetric methods [1].

There are substances able to rotate the polarization plane of the light because of their molecular or crystalline structure lacks symmetry: they are called optically active materials. Sugar solutions and crystalline quartz present this property. The polarization rotation is proportional to the number of molecules in the pathway of the radiation of the light. In the case of sucrose solutions, the polarization rotation depends on the concentration, the length of the containing tube, the temperature and the wavelength of the radiation. Following the reference [1], "the "normal sugar solution" is defined as 26.0160 g of pure sucrose weighed in vacuo and dissolved in water at 20.00°C to a final volume of 100.000 cm³. This corresponds to 26.000 g weighed in air under normal conditions (1013 mbar, 20°C, 50% relative humidity) and dissolved in water to a final volume of 100.000 cm³".

Based on the International Sugar Scale (ISS) [2, 3], the 100°Z point corresponds to the optical rotation of the normal solution of pure sucrose at the wavelength of the green line of the mercury isotope ¹⁹⁸Hg (546.2271 nm in vacuo) at 20.00°C in a 200.000 mm tube. For other wavelengths the formula for rotatory dispersion of sucrose solutions is valid [4]. The formula (presented as equation 3) is valid at the wavelength range from 546 nm to 900 nm, for practical polarimetry, and resulted from fittings of accurate measurements since 1961 to 1998 [5, 6, 7], starting at the visible region of the spectra and later extended to the NIR region. These measurements included rotation dispersion for quartz as well, and now constitute the Official Specifications from ICUMSA [1] and OIML [8] for the ISS. Crystalline quartz can be used as a standard material, to which any measurement of sugar solution is compared, a so-called quartz control plate.

Biot's Law equation

The Biot's Law for optical rotation is the basis of the sugar polarimetric measurements. The optical rotation in angular degrees is proportional to the specific rotation, sucrose concentration and the tube length:

$$\alpha_{\lambda}^t = [\alpha]_{\lambda}^t \cdot c \cdot l \quad (1)$$

Where:

α_{λ}^t is the optical rotation in angular degrees

$[\alpha]_{\lambda}^t$ is the specific rotation in angular degrees per dm and per g/cm³, dependent on the temperature and the wavelength

t is the temperature in °C

λ is the wavelength in nm

c is the concentration of sucrose in g/cm³

l is the length of the polarimeter tube in dm

The ISS fixed by convention the values of $t = 20.00$ °C, $l = 2.00000$ dm = 200.000 mm, $c = 0.260160$ g/cm³ = 26.0160 g/100.000 cm³.

Concentration and temperature dependence

The dependence of the optical rotation on concentration and temperature was derived from precision measurements [5, 6]. Those results were updated to the International Temperature Scale of 1990, and extended to the NIR region of wavelengths [7]. This dependence is fixed for the mass fraction $w = 0 - 0.65$ and the temperature $t = 18 - 30$ °C. This equation is valid for the standard wavelength of $\lambda = 546.2271$ nm.

$$\alpha_{546} = a_{01}w + a_{02}w^2 + a_{03}w^3 + a_{04}w^4 + a_{05}w^5 + (a_{11}w + a_{12}w^2 + a_{13}w^3) \cdot (t - 20) \quad (2)$$

Where:

w is the mass fraction in g sucrose/g solution (i.e. a decimal fraction; elsewhere it may be expressed as a %)

t is the temperature of the solution in °C.

$$a_{01} = 156.3547156 \quad a_{02} = 61.649313$$

$$a_{03} = 18.207098 \quad a_{04} = 7.1668107$$

$$a_{05} = -13.233339 \quad a_{11} = -5.6904146 \times 10^{-2}$$

$$a_{12} = -1.2240926 \times 10^{-1} \quad a_{13} = 7.7957582 \times 10^{-2}$$

For the standard conditions, the optical rotation α_{546} obtained from equation (2), corresponding to the 100°Z point of the ISS at visible wavelengths, is:

$$\alpha_{546.2271nm}^{20.00^{\circ}C} = 40.777 \pm 0.001^{\circ}$$

Wavelength dependence

The dependence of the optical rotation on wavelength was determined from experimental data of reference [7], and officialized by the Subject 4 ICUMSA report [4]. The rotation of sucrose solution α , at a wavelength λ (in μm), is calculated using the value for 0.5462271 μm , α_{546} :

$$\alpha_{\lambda} = \frac{\alpha_{546}}{a_0 + a_1\lambda^2 + a_2\lambda^4 + a_3\lambda^6} \quad (3)$$

Where:

$$a_0 = -0.075047659 \quad a_1 = 3.588221904585$$

$$a_2 = 0.0519461783 \quad a_3 = -0.006515194377$$

This formula for practical polarimetry is valid at the wavelength range from 546 nm to 900 nm.

The commercial saccharimeters are assembled with different light sources, and the used wavelengths are regulated under the ICUMSA standards. The 100°Z point of the ISS at those wavelengths are calculated using equations (2) and (3) combined, yielding,

for light of quartz wedge instruments:

$$\alpha_{587.0000nm}^{20.00^{\circ}C} = 34.934 \pm 0.001^{\circ}$$

for yellow sodium lines:

$$\alpha_{589.4400nm}^{20.00^{\circ}C} = 34.626 \pm 0.001^{\circ}$$

for He-Ne laser:

$$\alpha_{632.9914nm}^{20.00^{\circ}C} = 29.751 \pm 0.001^{\circ}$$

Nowadays there are saccharimeters with NIR radiation available, but their wavelengths are not rigorously established by ICUMSA like those mentioned above. In this case, the used NIR wavelengths by the industry need to be accurately determined in order to calculate the optical rotation corresponding to the 100°Z point from equation (3).

The quartz control plates

Quartz crystals are constituted by SiO₂ and the most stable structure is the trigonal, the α-quartz. Their physico-chemical properties turn the material very stable, and the optical properties has made the quartz the best choice for a standard, instead of the sucrose solutions. For example, sucrose solutions are not so stable over the time: they can evaporate, suffer chemical modifications, and be attacked by fungi and bacteria. Furthermore, its optical rotation value is very sensitive to the variations of temperature, while quartz is less sensitive. For this reason, to fulfill the requirements of the statutory authorities or the trade for absolute measurements, the polarimeters must be calibrated using the quartz plate standards, by specialized laboratories who can issue a calibration certificate. Crystalline quartz plates cut vertically to the crystal axis, of specified dimensions and constructions [9], so that its optical rotation at 20.00°C matches the optical rotation of a “normal sugar solution” under standard conditions has a value of 100.00°Z for a wavelength of 546.2271 nm, and are called “normal” plates. When another wavelength different from 546.2271 nm is used, a quartz plate has a sugar value of 100.00°Z only if its optical rotation has the same value of the optical rotation of a normal sucrose solution for that wavelength. This is why the quartz control plates are manufactured in order to present 100.00°Z for a particular wavelength. For others wavelengths, it is necessary to know the specific rotatory dispersion of quartz.

Dispersion equation

The specific rotation dispersion of quartz as determined from experimental data [6] and from the 22nd Session study [4], is shown below and is valid in the range 546 - 900 nm.

$$[\alpha] = a_0 + \frac{a_1}{\lambda^2} + \frac{a_2}{\lambda^4} + \frac{a_3}{\lambda^6} \quad (4)$$

Where:

$[\alpha]$ is the specific rotation of quartz in °/mm

λ is the wavelength in μm

$$a_0 = -0.1963657 \quad a_1 = 7.262667$$

$$a_2 = 0.1171867 \quad a_3 = 0.0019554$$

For example, for a plate that shows 100°Z for 546.2271nm, the optical rotations for other wavelengths are as follows:

$$\alpha_{546.2271nm}^{20.00^\circ C} = 40.777 \pm 0.001^\circ$$

$$\alpha_{589.4400nm}^{20.00^\circ C} = 34.692 \pm 0.001^\circ$$

$$\alpha_{632.9914nm}^{20.00^\circ C} = 29.846 \pm 0.001^\circ$$

Temperature dependence

Although much smaller compared to the sugar solutions, there is a dependence of the rotation with the temperature for quartz, which generates a correction factor when the measurement is realized at temperatures different from the normal temperature 20 °C.

The temperature dependence of the rotation for quartz was evaluated and fitted to the formula below, in which λ is the wavelength (in μm) and $\alpha_{20^\circ C}$ is the rotation at 20 °C [4].

$$\frac{\alpha_{t^\circ C}}{\alpha_{20^\circ C}} = 1.0 + \left(a_1 + \frac{a_2}{\lambda} + \frac{a_3}{\lambda^2} \right) \cdot (t - 20) \quad (5)$$

With:

$$a_1 = 1.280924 \times 10^{-4} \quad a_2 = 1.0852636 \times 10^{-5}$$

$$a_3 = -9.0311692 \times 10^{-7}$$

The experimental setup at Inmetro

The ICUMSA [1] and the OIML [8] Officially state the conditions of a polarimeter for quartz plate calibration. The plates themselves are subjected to regulations [1]: they are discs measuring between 15 and 17 mm in diameter, with a thickness of no more than 1,6mm and that shall not vary by more than 0.15 μm over the whole area of the plate. Each surface shall lie between two imaginary parallel planes 0.5 μm apart. The angle between the optical axis and that normal to the faces shall be less than 10 angular minutes. Besides, the quartz needs to have purity and be free of inclusions and cracks. Optical properties of a quartz plate may change under stress, for example, introduced by mishandling at the sugar factories laboratories. The first thing before polarimetric calibration is a thorough examination on the physical conditions of the plate: verify parallelism of the faces and optical axis error, flatness, absence of scratches, and optical purity. Next step is measuring the optical rotation at a precision polarimeter and give the result in a calibration certificate.

The basic polarimeter consists of a monochromatic light source, a polarizer, a sample cell/holder, a second polarizer, which is called the analyzer, and a light detector. At first, without sample, the analyzer is oriented 90° to the polarizer and thus no light reaches the detector. When the sample is placed between the two crossed polarizers, it rotates the polarization of the light reaching the analyzer, so that there is a component that reaches the detector. The angle that the analyzer must be rotated to return to the minimum detector signal is the optical rotation α .

ICUMSA [1] and the OIML [8] recommends that the wavelength of the incident light must be very well known up to 10⁻⁴ nm, the temperature must be controlled in order to stay under 20.00±0.01°C, and the polarization rotation angle must be determined with an accuracy of 0.0003°. A high precision polarimeter at PTB is the one in use for quartz plate reference calibration services [5, 6]. Based on that model, Inmetro as a National Metrology Institute is building a similar set-up in Brasil, in order to provide the traceability chain.

Figure1 shows a diagram of the first prototype of a polarimeter that is being set up at Inmetro. The light source (L) is a He-Ne laser with $\lambda = 632.9914$ nm. The first Glan-Thompson calcite polarizer (P1) is mounted on a manual

graduated rotary stage, where the P1 polarization axis is parallel to the polarization plane of the laser. A second Glan-Thompson calcite polarizer (P2) is mounted on another manual graduated rotary stage, and is rotated in order to have a “zero” transmission. The quartz plate (Q) is positioned between both polarizers, and the light that comes through is detected at a Si diode detector (D) connected to a multimeter. A platinum resistor Pt100 sensor (T) monitors the temperature close to the quartz plate. The Faraday Modulator (FM) and the lock-in purposes are explained later.

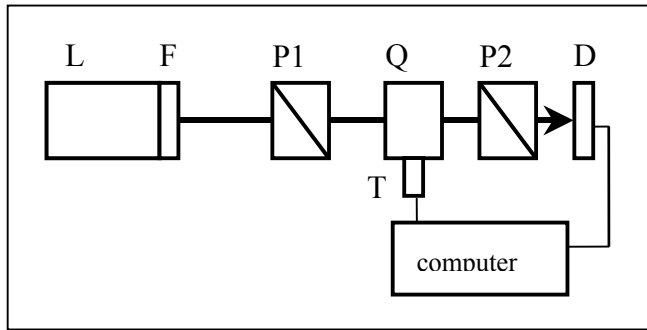


Figure 1: Diagram of the prototype of a polarimeter at Inmetro.

The detailed description of the equipment used in the set-up is presented below:

L: linearly polarized He-Ne laser, from Melles Griot, model 25-LHP-151-249;

P1 and P2: Glan Thompson calcite polarizers, from Newport, model 10GT04;

Q: quartz control plate, manufactured to have 100°Z at $\lambda = 632.9914 \text{ nm}$, ($\alpha = 29.751^\circ$);

D: Si low power detector from Newport, model 818-UV;

Graduated rotary stages: from Newport, model M-481-A, with 30 arcsec resolution;

F29 and F30: metallic neutral density filters, from Newport, model FBR-ND-F29 having 50.1 % and FBR-ND-F30 having 31.6 % of transmission at 633nm.

Preliminary tests and rough measurements with these available equipments were realized, where the intensity from D and temperature from T are visually read by a human operator and written down at a paper notebook. Later on, the data is entered at a graphical data analysis software. The procedure is monitoring the light intensity after adding each individual optical element.

The output of the 5 mW laser needs to be attenuated because of the detector threshold: it is used a F29 and a F30 neutral density filters right after the laser output. A black cover encloses all the set up, and thin openings are left above the polarizer rotators, in order to read the dials. The background noise is measured with all the laboratory lights turned on, half-turned on and all turned off. The result of half the laboratory lights turned on and all lights off is practically the same. This last condition is chosen to realize the experiment.

As a first step, P1 has to be parallel to the polarization plane of the laser. To achieve this condition, P1 is rotated at selected angular steps, and at each angular step the intensity at D, and the reading at T is annotated. This procedure was repeated several times at 5° angular steps: the intensity versus angular position showed an oscillatory pattern, with

their maxima and minima alternating at 90° . The manual rotator has a vernier (fine adjustment) with 0.02° angular steps, in a range of 5° . After choosing one of the angular position of minimum intensity, a screw fixes the large dial and the measurements is realized from $-2.5^\circ \leq$ angular position of minimum $\leq +2.5^\circ$ with 0.02° angular steps. An amplification lens helps on the reading of the dial. The angular position corresponding to the minimum intensity of P1 is determined, and thus the angular position of the maximum intensity was obtained by adding 90° . This was more accurate than determining the maximum intensity directly. At this stage, P1 is parallel to the laser output polarization plane.

As a second step, the angular position of P2 has to be find so that P1 and P2 are polarization crossed, where, ideally, no light comes through the detector; but due to the finite extinction ratio of the polarizers, some “minimum intensity” can be measured. With P1 fixed, the same procedure of the first step is done with P2, in order to find the angular position of minimum intensity. After that, the quartz plate Q is positioned between P1 and P2: this leads to the rotation of the polarization plane of the light, and the intensity detected at D increases. In order to determine the rotation angle, P2 is turned up to a new minimum detection. The third step is the precise determination of this new minimum position of P2, using the large dial at 5° steps and the vernier 0.02° fine steps. In order to find that minimum with accuracy, the sequences of measurements are repeated 10 times. The position of each minimum is found after adjusting the experimental data to a polynomial function, using a non-linear curve fitting procedure. The rotation angle α due to the insertion of the quartz plate is then obtained calculating the difference between the two minimums, corresponding to the measurements with and without the quartz control plate.

Considering the case with the quartz control plate, and with measurements done at $t = 25.86^\circ\text{C}$, figure 2 shows an example of the results of the fitting to the data, using a second degree polynomial function adjusted in the range $104.8^\circ - 105.7^\circ$:

$$y = 11641.9508 - 221.17904 \cdot x + 1.05055 \cdot x^2$$

The minimum angular position obtained from the curve is:

$$y_{\min} = -\frac{B1}{2A} = 105.27^\circ$$

A similar fit curve is obtained in the case without the quartz plate, and the minimum calculated is: 133.66° . Then the difference deduced between the two minimums is:

$$\alpha = 28.39^\circ$$

Applying equation (5), the expected value for the optical rotation at the mentioned temperature t is:

$$\alpha_{632.9914}^{25.86^\circ} = 29.776^\circ,$$

which lead to the huge discrepancy of 1.38° .

The biggest drawback of the measurement is the backlash of the polarization rotator: after 10 sequences of

measurements, the minimum position has changed from 105.268° to 105.456° , which gives 0.188° difference. This discrepancy is not correlated so much to temperature fluctuations in the room, since the measurements spanned several days. As an example of the relatively small effect of t on the optical rotation measurements of the quartz plate, the comparison between $\alpha_{632.9914}^{20^\circ} = 29.751^\circ$ and $\alpha_{632.9914}^{25.86^\circ} = 29.776^\circ$ lead to a difference of 0.025° over 5.86°C . This value is relatively small comparing to the measured dispersion of the minimum positions. Therefore, the deviation of 1.38° is, at least, due to the backlash of the polarization rotator.

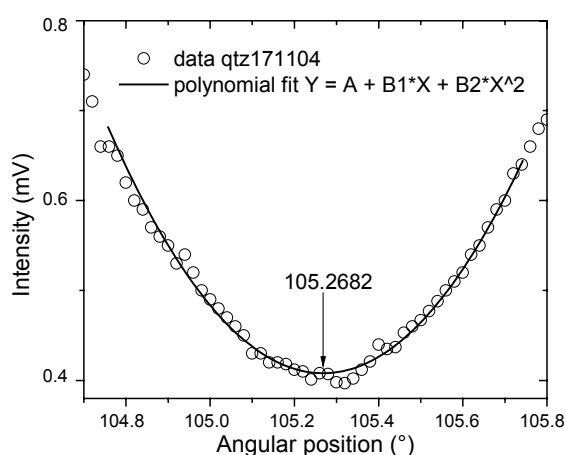


Figure 2: Example of a polynomial fitting to the experimental data.

As said before, such preliminary and rough measurements show that a lot of work has to be done on our experimental set up. As an improvement of the measurement procedure, it is being considered the use of a high precision programmable motorized rotator with an encoder to substitute P2, a method already used in a set up for a rotating-polarizer polarimeter for accurate retardance measurement [10]. Another necessary improvement is to have all the data acquired by a computer program, where the temperature and the laser intensity can be simultaneously read with repetitions for statistics. The inclusion of a Faraday modulator for the light polarization modulation and a lock-in amplifier is the next necessary step. The temperature of the laboratory should be controlled at $20 \pm 0.1^\circ\text{C}$, and a fine thermal stabilization might control an enclosure of the quartz plate and probably the polarizers too. A stabilized He-Ne laser is to be used also in the improvement of the set up.

Conclusion

It has been stated the political and economical necessities of assembling a calibration system for quartz reference plates used in the Brazilian sugar industry. It has been considered the status of the official statements and recommendations from the international organizations that regulate the sector.

The first attempt of an experimental set up at Inmetro has been reported, and improvements are under way.

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