CALIBRATION OF NIR POLARIMETERS

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Abstract

Polarimetry is one of the basic methods used for factory control and payment systems in the sugar industry. One of its benefits is that the instrument can be calibrated using certified standards. This enables factory staff, buyers and sellers to check polarimeters at any time and, in the case of controversies, independent boards can verify disputed results.

The increased awareness of environmental and health issues makes it desirable to avoid the use of basic lead acetate for sample clarification. Instruments using near-infrared light (NIR polarimeters) can measure samples directly after filtration, making these instruments increasingly more important. Initially the problem was that the calibration procedure for polarimeters given by ICUMSA prior to 1998 was based on measurements with visible light only. Although NIR polarimeters could be calibrated to give reproducible results, the scientific foundation was missing.

In co-operation between the German Physical State Laboratories (PTB), the Sugar Institute in Braunschweig and the company Schmidt & Haensch, a new procedure has been developed, which was officially adopted at the ICUMSA meeting in Berlin in 1998.

With the new procedure the readings of NIR polarimeters will be higher by 0,06% than those achieved with the former method. This paper deals with the practical implication of this change.

Introduction

One of the main advantages of polarimeters over alternative methods for sugar analysis is that these instruments can easily be calibrated using certified standards. This makes it possible for both the sugar factory and the farmers to base payment upon a reliable polarimetric value of a sample.

A disadvantage in the past has been that standard polarimeters were not able to cope directly with dark samples such as molasses and syrup. These samples needed to be 'clarified' with basic lead acetate first. With the introduction of NIR polarimeters in the 1980s it became possible to measure non-clarified samples in the sugar industry, as they show a rather low absorbence in the NIR. This has been a significant improvement, as the treatment with basic lead acetate should be avoided for safety and environmental reasons.

Polarimeters in the sugar industry are configured to display in the International Sugar Scale. The 100,00°Z point of this scale is defined as the reading of the Normal Sugar Solution, i.e. 26 g of pure sucrose, dissolved in distilled water to 100 cm^3. For the calibration, quartz plates are used instead of sugar solutions, as they can be certified by the Physikalisch Technische Bundesanstalt (PTB), which is the highest technical authority in Germany for the field of metrology. The calibration can thus be done impartially.

At the PTB, the correct reading of these plates in sugar degrees (°Z) is evaluated by measuring their value at one precisely known wavelength. The readings at other wavelengths are derived from this value using formulae based on the influence of the wavelength on the polarimetric readings of quartz and sucrose. Until 1998, the officially used formulae for this were based on measurements with visible light only. The ICUMSA recommended their use even for NIR polarimeters (Proc. 20th Session of ICUMSA, 1990, 206), although works by Altenburg and Chou (1991) and Paton *et al.* (1993) indicated that following this recommendation the readings of pure sucrose solutions in NIR polarimeters were 0,06% lower than those in standard polarimeters.

This was the reason for the PTB, the Sugar Institute in Braunschweig and the company Schmidt & Haensch to make precise measurements using NIR polarimetry, leading to a paper by Emmerich *et al.* (1998). The results were presented and officially adopted at the 1998 Session of the ICUMSA in Berlin, and the ICUMSA Methods Book was revised accordingly.

Discussion

Rotation of quartz

The angular rotation of polarised light (α), induced by a quartz plate of 1 mm thickness at a wavelength λ (in μm) can be calculated as follows:

$$\alpha = -0{,}1963657 + 7{,}262667 \cdot \lambda^{-2} + 0{,}1171867 \cdot \lambda^{-4} + 0{,}0019554 \cdot \lambda^{-6}$$

In the visible region there is no difference between the old and new formulae, while there is a slight deviation in the NIR region:

$$\alpha(882{,}6\ \text{nm, old}) = 9.323°$$

$$\alpha(882{,}6\ \text{nm, new}) = 9.324°$$

The temperature effect is very similar in the visible and the NIR, with values of

$$\alpha_{t°C} / \alpha_{20°C}\ (\text{VIS}) = 1{,}0 + 0{,}000144 \cdot (t - 20)$$

$$\alpha_{t°C} / \alpha_{20°C}\ (\text{NIR}) = 1{,}0 + 0{,}000139 \cdot (t - 20)$$

Rotation of sucrose

For sucrose the angular rotation of polarised light (α) at a wavelength λ (in μm) in relation to that of the same solution at 546,2271 nm (α_{546}) is described by the following formula:

$$\alpha_\lambda = \alpha_{546} / (a_0 + a_1 \cdot \lambda^2 + a_2 \cdot \lambda^4 + a_3 \cdot \lambda^6)$$

$$a_0 = -0{,}075047659$$

$$a_1 = 3{,}588221904585$$

$$a_2 = 0{,}0519461783$$

$$a_3 = -0{,}006515194377$$

For the Normal Sugar Solution (26 g to 100 cm³) the correct value is the well known:

$$\alpha_{546} = 40{,}777289°$$

Again, there is no difference between the new formula and the old in the visible region, but in the NIR region the values are:

$$\alpha(882{,}60\text{ nm, old}) = 14{,}844°$$

$$\alpha(882{,}60\text{ nm, new}) = 14{,}836°$$

This is a difference of 0,06%.

The change with the temperature is slightly higher in the NIR region than in the visible:

$$\alpha_{t°C} / \alpha_{20°C}\ (\text{VIS}) = 1{,}0 - 0{,}000474 \cdot (t - 20)$$

$$\alpha_{t°C} / \alpha_{20°C}\ (\text{NIR}) = 1{,}0 - 0{,}000493 \cdot (t - 20)$$

The validity range of these new formulae for practical polarimetry is 540 to 900 nm.

Quartz wedge saccharimeter

Quartz wedge saccharimeters have been well established in the sugar industry for decades. The special advantage is that these instruments, in contrast to all other polarimeters, do not need regular re-calibration. Today, quartz wedge saccharimeters are available not only for the well known yellow wavelength, but also for the NIR (882,60 nm).

Implications for the calibration

The calibration procedures for all polarimeters using *visible* wavelengths do not have to be changed. The changes only apply to polarimeters working in the NIR. If a quartz plate of 100,00°Z at 589,44 nm (the standard wavelength for polarimeters) and a Normal Sugar Solution are measured in a standard polarimeter and in a NIR polarimeter calibrated using the old and the new procedures respectively, the readings will be as follows:

	589,44 nm	882,60 nm old formula	882,60 nm new formula
Quartz Plate	100,00 °Z	100,11 °Z	100,17 °Z
Normal Sugar Solution	100,00 °Z	99,94 °Z	100,00 °Z

The result for the sugar solution is close to that found by Altenburg and Chou (1991) and Paton *et al.* (1993).

So, to change over to the new procedure, the calibration has to be done with a new set point for the quartz plate in sugar degrees. The valid reading for 589,44 nm has to be multiplied by 1,00174 to get the correct reading at 882,60 nm. The theoretical reading of a quartz in the NIR following the old procedure has to be multiplied by 1,00063 to get the correct reading following the new procedure.

It has to be kept in mind that both the old and new calibration procedures lead to reproducible results. Any contract based on the old procedure can stay as it is. The only objective in setting a new procedure is that it is closer to the definition, as the Normal Sugar Solution will show 100,00°Z in a NIR polarimeter calibrated using the new procedure.

Practical measurements

For measurements of samples such as first expressed juices or raw sugar solutions there will be a slight difference between the visible polarimeters and the NIR types, whether they are calibrated using the old or new procedure. This is because technical sugar solutions do not contain only sucrose, but also some other ingredients which influence the reading. This is especially valid for first expressed juice. The clarification used in the visible polarimeters changes the composition slightly, and the wavelength effect on other ingredients may vary from that on sucrose.

In the case of raw sugars the reading in NIR polarimeters is typically slightly lower than in conventional polarimeters. This is the volume effect of the sample preparation. The 26 g of sugar is transferred to a flask and water added to about 60 to 70 ml. Before the flask is made to the mark, the lead acetate solution is added. With the clarification the volume is increased by the precipitate, and the amount of water added is therefore somewhat smaller than without clarification. That is why the concentration of clarified samples is slightly higher than that of non-clarified samples.

With the new calibration procedure pure sucrose solutions will be measured according to the definition of the International Sugar Scale; but technical sugar solutions may still have different results when measured with NIR polarimeters than those measured conventionally. For this reason more comparative tests are necessary before NIR polarimetry can be regarded as a standard method.

Filtration

The proper filtration of samples is crucial for all polarimeters. In the case of non-clarified samples this may be a problem, as basic lead acetate is also a powerful filtration aid. That is why a normal gravity filtration is usually sufficient for clarified samples. This is not true for some of the non-clarified samples. In the sugar industry it is very important to use filtration techniques which combine easy handling with a short filtration time and an efficient way to avoid cross contamination of samples, as high sample rates are typical.

Recent tests in Thailand have proven that a special pressure filtration unit designed for the sugar laboratory by Schmidt & Haensch gives satisfactory results on first expressed juices.

Conclusion

With the new calibration the reading of NIR polarimeters will be 0,06% higher than with the old method. From a technical point of view the temperature effects are the same for the visible and the NIR. However, before the NIR polarimeters can be used as standard instruments, more collaborative testing is needed.

For the filtration of non-clarified samples, new techniques are available which are satisfactory in terms of filtration time, performance and handling.

REFERENCES

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