TRANSITION FROM LEADED POL TO NIR POL IN THE SOUTH AFRICAN SUGAR INDUSTRY

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Abstract

The South African sugar industry is facing a change from the conventional, lead-based pol analyses to the use of a lead-free pol method in the 2003/04 season. The new method involves the use of a near infrared (NIR) light source which does not require the test solution to be of low colour. Lead clarification can therefore be replaced by a simple filtration step to remove solution turbidity. Lead sub-acetate clarification is known to complex non-sucrose components such as fructose, glucose, dextrans and colourants in solution; the simple filtration needed for NIR pol, using a suitable filter aid, does not alter the chemical composition of the test solution. The effects of seasonal trends in terms of the concentration of these non-sucrose components on the NIR pol values of various products are not yet fully established and difficult to predict.

The phased transition from the use of conventional pol to NIR pol is therefore being scrutinised to identify any possible pitfalls. An attempt is also made to approximate the effect of NIR pol on important South African factory performance measures, and to present some guidelines on the interpretation of NIR pol values.

Keywords: analysis, polarimetry, lead, near infrared polarimetry, pol, sucrose

Introduction

The sugar manufacturing industry has, since 1842, relied on polarimetry as a measure of sucrose content in crops, factory and refinery products. Polarimetry is a rapid, precise but indirect measurement to quantify the amount of sucrose in the sample. It is affected by other optically active components such as glucose, fructose and dextrans present in the sample. The speed, ease of use and reproducibility of pol readings have supported its continued use in the sugar industry; the accuracy of the pol reading as it relates to the true sucrose content has often been a secondary issue.

Increased health and environmental concerns associated with the use of lead for sample clarification has put pressure on the use of conventional leaded pol analysis. Various alternatives have been investigated world-wide to avoid the use of lead, such as Octapol (van Staden and Mdlalose, 2000), bismuth chloride (Huang, 1985), XYZ-clarification agent (Gao *et al.*, 2000), various aluminium reagents (Simpson and Corica, 1997), combined calcium and aluminium compounds (Chou, 1987) and zinc salts (Auth and Rearick, 1989). While some of the clarification agents showed potential, none of them could clarify dilute molasses to a satisfactory level. The most promising and presently tested alternative is the use of NIR polarimetry (Altenburg and Chou, 1991; Wilson, 1995). A method for the analysis of pol in sugars, based on this technique, has already been developed and was accepted by ICUMSA in 1999 (Player *et al.*, 2000; Anon, 1999).

Fundamental pol principles

Sucrose is a dextrorotatory optically active compound; it rotates the plane of a passing polarised light wave to the right, i.e. in the positive direction by convention. In solution, the angle of rotation of the polarised light caused by the sucrose is a function of the sucrose concentration. The sucrose content measured by a polarimeter using this phenomenon is called 'pol'. Other compounds in typical sugar mill factory products such as fructose, glucose and dextrans are also optically active, with their ability to cause optical rotation being a function of their respective concentrations. Each optically active substance has its own specific rotation as defined by Biots law (Equation 1) (Bates, 1942).

$$[\alpha]_{\lambda}^{T} = \frac{\alpha_{\lambda}^{T}}{c \times l} \qquad (1)$$

where $[\alpha]$ = specific rotation
l = optical path length in dm
λ = wavelength
T = temperature
α = optical rotation
c = concentration in g/cm^3

By definition, a solution containing 26.000 g sucrose in 100.000 cm^3 at 20°C in a 200 mm pol tube, will have an optical rotation of 34.626° at 589.44 nm (Player *et al.*, 2000). The specific rotations of some sugars together with their optical rotations are indicated in Table 1.

Table 1. Optical rotations of some standard sugar solutions.

SUGAR	**Specific rotation (°)**	**Optical rotation (°)**
Sucrose	+ 66.59	+ 34.626
Glucose (without concentration correction)	+ 52.50	+ 27.3
Fructose (without concentration correction)	- 91.33	- 47.49
Dextrans (polysaccharides)	+ 195 to + 205	+ 101.4 to + 106.6

The net rotation of the plane of light by a solution containing more than one optically active component is equal to the sum of the rotational effects of the individual components. Glucose and dextrans turn the plane clockwise (dextrorotatory), and fructose anti-clockwise (laevorotatory). Pol is therefore defined as the apparent sucrose in a solution and is used as if it was a real substance (Anon, 1985). In general, the lower the purity of the sample, the greater the difference between the pol reading and the true sucrose (Bates, 1942; Browne, 1941; Browne and Zerban, 1948; Meade and Chen, 1977).

The observed optical rotation of certain sugars such as glucose and fructose may change over time. These sugars have four different isomers in solution and the phenomenon is explained by the equilibration between these isomers over time, termed 'mutarotation'. Only one isomer of sucrose exists and a pure sucrose solution does therefore not display this effect. Although mutarotation in sugarcane factory products has not yet been extensively investigated, it should not be of much concern when measuring pol, due to the relatively low levels of glucose and fructose in these products (Simpson and Corica, 1997).

Any suspended matter in the solution causes scatter of the polarised light and interferes with the measurement of the angular rotation. To avoid this, the sample solution must be filtered so as to be clear before being measured. A conventional polarimeter uses a light source in the visible spectrum at a wavelength of 589 nm (yellow, chosen for its high intensity). Even at this wavelength the colour of the solution affects the transmittance of the light through the solution. Colour is therefore traditionally removed from solution using lead sub-acetate as a clarification agent. The maximum absorbance at 420 nm of solutions that can be read on a conventional polarimeter is 0.17 (*ca.* 270 IU without pH adjustment) (Paton *et al.*, 1993), above which the reading becomes unstable.

Together with colour components, lead sub-acetate also removes about 11% of the fructose (while reducing the laevorotation of the remaining fructose) (Meade and Chen, 1977) and roughly two-thirds of the high molecular weight (HMW) dextrans present (Bradbury *et al.*, 1986). It would be incorrect to assume that lead does not remove any sucrose and glucose, although the effect is insignificant with small amounts of lead used (Bates, 1942). However, the various quantities that are removed by lead clarification vary to a large degree, depending on the amount of lead used and on the composition of the sample (Paton *et al.*, 1993; Simpson and Corica, 1997). Many mineral salts are also believed to change the specific rotation of sucrose by complex formation, while certain acids may increase the specific rotation of some sugars (Meade and Chen, 1977; Browne, 1941).

The optical rotation of a substance is an exact function of its concentration under the conditions of analysis. An equation to describe the pol value when considering sucrose, fructose and glucose (and sometimes kestose) only, based on their optical rotation-concentration functions, is often used to calculate an expected pol value, known as 'pol derived'. A strong correlation between pol and pol derived, indicative that the main non-sucrose contribution to pol comes from fructose and glucose, was found (Morel du Boil and Schäffler, 1978a, 1978b). This equation was subsequently updated for closer approximations and to calculate pol in °Z instead of °S (Equation 2) (Anon, 1998).

$$\text{Pol derived} = S + [(52.50 + 0.005902 * G + 1.4872\text{E-}5 * G^2) * G + (-91.33 - 0.04264 * F + 5.8136\text{E-}5 * F^2) * F] / 66.59 \quad (2)$$

where S = sucrose (mass % sample)
G = glucose (mass % sample)
F = fructose (mass % sample)

Although the main non-sucrose contribution to pol comes from fructose and glucose, optically active components other than fructose and glucose will also have an effect on the final pol value. For example, dextrans have specific rotations in a range much higher than that of sucrose (refer to Table 1) and the pol value will therefore increase when dextran levels are prominent. Since Equation 2 does not account for the effect of non-sucrose components other than fructose and glucose, the difference between the pol and pol derived values can be used to flag the presence of dextrans, mineral salts, acids or microbiological activity.

Pol derived values will further differ from pol values when using lead sub-acetate as clarification agent since the pol derived calculation is based on the amount of fructose and glucose in solution (as determined by chromatography) before alteration of the sample composition by lead clarification. These differences have, however, been monitored, and Equation 2 is often used as a standard check against experimental pol values where the differences should not exceed a predetermined value (e.g. 5 units in the case of molasses, refer to Table 2).

Table 2. Molasses lead pol values for 2002/03 season.

Lead pol (%)	Pol derived (%)	Lead pol - pol derived
28.88	26.05	2.83
27.69	25.34	2.35
30.45	26.80	3.65
30.00	26.41	3.59
28.39	24.42	3.97
29.82	26.29	3.53

NIR Polarimetry

The term near infrared (NIR) refers to a specific range of wavelengths in the electro-magnetic spectrum, normally between 800 and 2 000 nm. NIR is not a method, but is used in a number of analytical techniques such as spectroscopy, refractometry and polarimetry. These are very different techniques and it is important to distinguish clearly between them, even if they make use of similar wavelengths.

Modern NIR polarimeters typically use a near infrared light source at a wavelength of 882.6 nm. These lightwaves are able to travel through highly coloured solutions because the colour components do not absorb light at this wavelength, thus eliminating the need for colour removal. Since no optically active components are removed, this method has the added advantage that it gives a pol reading corresponding to a solution that is not chemically altered in any way. It is for this exact reason that there are differences between conventional leaded pol and unleaded NIR pol. NIR pol values are in general lower than leaded pol values, because the higher level of fructose present in the solution in the absence of lead clarification adjusts the angular rotation to the left, i.e. in the negative direction (laevorotatory) (Crees and Brotherton, 1991; Anon, 1999). Naturally, products with higher reducing sugar content will be more affected.

Table 3 shows the differences between measured NIR pol and pol derived values (refer to Equation 2) of molasses for different factories in the 2002/03 season.

Table 3. Molasses NIR pol values for 2002/03 season.

NIR pol (%)	Pol derived (%)	NIR pol - pol derived
26.48	27.36	˜0.84
27.96	27.21	0.79
29.41	28.05	1.38
26.47	25.70	0.80
31.41	31.65	˜0.22
29.06	28.99	0.09

Since the concentrations of fructose and glucose in the sample are not altered prior to pol reading, the pol derived value should be much closer to the experimental NIR pol than was the case with leaded pol (refer to Table 2). Equation 2 should therefore be used as a standard check against experimental NIR pol as soon as an acceptable level of the difference between the two values has been experimentally established.

Pol versus sucrose

Since 1982 (Schäffler and Day-Lewis, 1983), the major factory performance figures and overall cane payment in the South African sugar industry have been based on sucrose content measured by gas chromatography rather than pol. This procedure arose from the recognition that pol is not always a good estimate of sucrose (especially for low purity products). Together with the development of a suitable procedure for the determination of sucrose by gas chromatography, this led to the introduction of a system by which the sucrose content in weekly composite samples of mixed juice and final molasses is determined by chromatography in a central laboratory, together with pol values to generate a pol to sucrose ratio for each of the two products for every factory on a weekly basis, as illustrated in Table 4.

Table 4. SMRI mixed juice composite pol values and weekly pol to sucrose ratios (SMRI sucrose = 11.63%)

SMRI lead pol (%)	SMRI NIR pol (%)	SMRI lead pol/sucrose	SMRI NIR pol/sucrose
11.53	11.47	0.991	0.986

$$\text{calculated sucrose} = \frac{\text{pol}}{\text{pol/sucrose ratio}} \qquad (3)$$

This ratio is used to calculate the sucrose values from the factory pol readings, using Equation 3 as illustrated in Table 5. The calculated sucrose values are subsequently used for cane payment and factory control purposes. The mill calculated weighted average of the hourly sucrose values derived from the pol to sucrose ratios for each week should correspond to the central laboratory composite sucrose value for that mill (Anon, 1985; Brokensha *et al.*, 1978; Schäffler and Smith, 1978). (Differences will, however, exist between the mill and central laboratory sucrose values if the composite sample is not fully representative.)

Table 5. Mill hourly mixed juice pol and calculated sucrose values.

Lead pol (%)	NIR pol (%)	Calculated sucrose (%) (from lead pol/sucrose)	Calculated sucrose (%) (from NIR pol/sucrose)
11.58	11.52	11.68	11.68
11.24	11.19	11.34	11.34
11.75	11.69	11.85	11.85
11.47	11.41	11.57	11.57
11.59	11.53	11.69	11.69

Although the NIR pol values and the pol to sucrose ratios based on NIR polarimetry are different (usually lower) than the conventional leaded pol values, the derived sucrose content should be the same, provided that the correct pol to sucrose ratio (leaded pol or NIR pol) is applied to each pol value, as indicated in Tables 4 and 5.

Effect of using NIR pol on some factory products

Tables 6-8 illustrate expected differences between lead pol and NIR pol values for some factory products. These differences are averaged, and outliers or negative values can be expected.

Table 6. Averaged pol values for mixed juice (SMRI data 1999/2000 season).

Lead pol (%)	NIR pol (%)	Lead pol - NIR pol
12.24	12.19	0.04
11.34	11.32	0.02
11.07	11.04	0.03
10.45	10.41	0.04

Table 7. Averaged pol values for raw sugars (Paton *et al.*, 1993).

Lead pol (%)	NIR pol (%)	Lead pol - NIR pol
99.99	99.93	0.06
99.44	99.38	0.06
98.76	98.71	0.05
93.94	93.91	0.03

Table 8. Averaged pol values for molasses (SMRI data 2002/03 season).

Lead pol (%)	NIR pol (%)	Lead pol - NIR pol
30.51	26.75	3.75
31.04	27.93	3.11
31.97	28.96	3.01
33.77	30.07	3.70

Effect of NIR pol on cane payment

Although the distribution of proceeds between millers and growers will not be affected since it is based on sucrose, the redistribution of grower payments is based on pol and might be affected slightly. There have been some concerns with regards to deteriorated cane benefiting from the change to NIR pol because of the pol-boosting properties of the major deterioration products, namely HMW dextrans, which were partially removed by lead clarification.

However, Cox and Sahadeo (1992) found that sucrose in large burnt cane bundles deteriorates to form mainly fructose and glucose. High levels of laevorotatory fructose (more than 51 000 ppm on brix after 498 hours) which is no longer partially removed by lead when using NIR pol, should therefore largely counter-balance the inflating effects of increased levels of HMW dextrans (assumed to be no more than 3 000 ppm on brix) (Imrie and Tilbury, 1972) on NIR pol.

As a purely hypothetical illustration of the effect of HMW dextrans on leaded and NIR pol, typical sucrose, glucose and fructose values of expressed juice from fresh cane and from deteriorated cane were used together with a range of HMW dextran values between 90 and 3 000 ppm on brix to estimate corresponding pol values (refer to Tables 9 and 10). Lead clarification of the expressed juice is assumed to remove 66% HMW dextrans and 11% fructose from solution. Note that expressed juice from fresh cane does not usually contain HMW dextrans at the levels indicated.

Table 9. Hypothetical estimation of the effect of HMW dextrans on the pol of expressed juice from fresh cane. (based on sucrose = 17.64%, glucose = 0.08% and fructose = 0.09%)

HMW dextrans (%)	Estimated lead pol (%)	Estimated NIR pol (%)	*Lead pol - NIR pol*
0.001	17.60	17.59	0.01
0.006	17.61	17.61	0.00
0.011	17.61	17.62	-0.01
0.016	17.62	17.64	-0.02
0.021	17.62	17.65	-0.03
0.026	17.63	17.67	-0.04
0.031	17.63	17.68	-0.05

Estimated pol = pol derived + 3x dextrans (% mass) (Bradbury *et al*., 1986).
Estimated lead pol assumes removal of 11% fructose and 66% dextrans by lead.

Table 9 indicates that fresh cane with hypothetical high HMW dextran levels will inflate NIR pol as compared to lead pol. However, from Table 10 it is clear that NIR pol of deteriorated cane is already expected to be lower than leaded pol throughout. There is therefore certainly no incentive to allow cane to deteriorate purposely in the hope of benefiting from the pol-boosting properties of HMW dextrans when using NIR pol.

Table 10. Hypothetical estimation of the effect of HMW dextrans on the pol of expressed juice from deteriorated cane (498 h). (based on sucrose = 13.98%, glucose = 0.75% and fructose = 0.90%)

HMW dextrans (%)	Estimated lead pol (%)	Estimated NIR pol (%)	Lead pol - NIR pol
0.001	13.54	13.41	0.13
0.006	13.54	13.43	0.12
0.011	13.55	13.44	0.11
0.016	13.56	13.46	0.10
0.021	13.56	13.47	0.09
0.026	13.57	13.49	0.08
0.031	13.57	13.50	0.07

Estimated pol = pol derived + 3x dextrans (% mass) (Bradbury *et al*., 1986).
Estimated lead pol assumes removal of 11% fructose and 66% dextrans by lead.

Effect of NIR pol on some factory performance figures

Extraction, boiling house recovery and overall recovery are mainly sucrose-based and should not be affected by a change from the present method of pol analysis to the analysis by NIR pol. Any pol measurement used directly to calculate these recoveries is either very small (pol in bagasse) or is very close to the true sucrose (pol in sugar).

Sucrose balances and calculated figures, such as sucrose undetermined loss, that are based on sucrose content will not be affected by the use of NIR pol, provided that the pol values, be they leaded pol or NIR pol, produced by the mill are of the same type as the pol values used by the central laboratory for the calculation of pol to sucrose ratios.

Pol to sucrose ratios will drop typically from 0.991 to 0.986 for mixed juice and typically from 0.970 to 0.868 for molasses. This is to be expected since the sucrose values stay constant while the pol values are reduced.

Estimates of pol in stock, and hence stock purities, may drop when using NIR pol. However, this will not affect the end of season figures, once boil-off has been completed.

Additional inconsistencies can be expected in the interim period between factories using different methods of pol determination, or within a factory which uses different pol methods for different products. These should disappear as soon as the conversion to NIR pol is completed.

Financial implications of changing the analytical method

Apart from eliminating the use of lead, NIR pol will also have financial advantages. The total cost of consumables for a single sample will typically be R1.80 when using lead clarification and less than five cents when using NIR pol (Schoonees, 2003).

A note on convention

There needs to be a clear distinction between leaded pol figures, and NIR pol figures especially in the interim period. It is proposed that the subscript ‘Pb’ (pol_{Pb}) be used for pol with lead clarification and ‘NIR’ (pol_{NIR}) for NIR pol in the absence of lead clarification.

Conclusions

The decision of the South African sugar industry to move towards the elimination of lead in sugar laboratories emphasises its commitment to human health and the environment. A substantial amount of research has been invested in finding an alternative that is suited to the specific needs of the southern African sugar environment (van Staden and Mdlalose, 2000). Global trends tend strongly towards the use of NIR polarimetry; at least one of the major USA purchasing contracts has been based on the use of NIR polarimetry since 1993 (Altenburg *et al.*, 1994), and ICUMSA accepted a method for the use of NIR polarimetry on sugars in 1998 (Anon, 1999).

Because of the pol to sucrose ratio system used in South Africa (Anon, 1985), the use of NIR pol values will change the pol to sucrose ratio itself, but not the sucrose value. It will therefore have little or no effect on sucrose-based factory figures. Pol-based figures will be affected, the magnitude of which will depend on the type of products involved in the calculation.

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