

LEAD-FREE POL ANALYSIS USING NEAR INFRARED POLARIMETRY (NIRPOL)

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Abstract

Pol forms the basis of all sugar sales internationally. As a result of the perceived occupational health risks in addition to the problems and costs associated with the safe disposal of lead acetate (the clarifying agent used in conventional pol analyses), alternative methods of pol analysis are being investigated by the sugar industries world-wide. This investigation focussed on the use of NIR polarimetry for the determination of mixed juice pol. Weekly samples from four mills were analysed and the near infra-red pol (NIRPOL) results compared with both the lead acetate pol (LAP) and true sucrose (TSGC) results.

Introduction

A greater awareness of the occupational health risks and problems associated with the use and environmentally safe disposal of lead acetate world-wide, has resulted in numerous investigations into alternative methods of pol analysis this decade. In addition to evaluating alternative clarifying agents for pol analysis, new lead-free methods of analysis have been the focus of many research efforts (Crees, 1998; Boros *et al.*, 1996). A brief overview of the progress in this field from 1990 onwards is considered pertinent.

Instruments which operate at longer wavelength, *e.g.* in the laser (830 nm) (Clarke and Legendre, 1991; Simpson and Corica, 1997) or near infra-red (840 - 889 nm) regions are less sensitive to sample colour, as demonstrated by Paton and co-workers (1993). The advantage of a polarimeter operating in the near infra-red (NIR) region is that it would eliminate the undesirable lead acetate clarification (colour removal) step, simplifying the sample preparation to a filtration step for the removal of turbidity.

The similarity between the acronym NIR (near infra-red reflectance) and NIR (near infra-red) polarimetry has resulted in some confusion. It must be stressed that these are two distinct techniques, the former is a spectroscopic analysis, whilst the latter is a polarimetric (pol) measurement and therefore we will adopt the acronym NIRPOL for near infra-red pol/polarimetry without lead acetate clarification.

The first method employing this technology, *i.e.* the polarisation of raw sugar without basic lead acetate, was developed by Altenburg and Chou (1991). Comparisons of the results obtained in this study were complicated by the fact that different sugar scales were used for the measurements at 589 nm ($^{\circ}$ S) and 883 nm ($^{\circ}$ Z). Recalculation of the results reported by Altenburg and Chou (1991) indicated that the NIRPOL (883 nm) results were 0.066 $^{\circ}$ Z lower than the conventional lead acetate pol (LAP) results recorded at 589 nm (Emmerich, 1992 and Paton *et al.*, 1993). Emmerich (1992) reported that this dif-

ference is attributed to the extrapolation of Bünnagel's formula, which is valid in the 408 - 644 nm range, to the calibration/standardisation of polarimeters operating in the near infra-red region (840 - 890 nm).

Previous investigations have shown that lead acetate removes substantial amounts of dextran, which is not the case with celite filtration (Paton *et al.*, 1993). The presence of dextran, a dextrorotatory polysaccharide with an optical rotation three times that of sucrose, inflates pol readings. Paton and co-workers (1993) showed that the NIRPOL results are inflated and in better agreement with the LAP results for samples of similar pol, as the dextran levels increase (Table 1). As a consequence the differences between the NIRPOL and LAP results are more pronounced for raw sugars with low dextran levels. The drawback of this NIRPOL method is therefore, that the dextran levels will affect the raw sugar pol results more significantly than with the conventional LAP analysis at 589 nm.

Table 1. The effect of dextran on raw sugar pol reported by Paton *et al.* (1993).

LAP ₅₈₉ / $^{\circ}$ Z	NIRPOL/ $^{\circ}$ Z	NIRPOL - LAP ₅₈₉ / $^{\circ}$ Z	Dextran/ppm
97.62	97.47	- 0.15	425
97.61	97.55	- 0.06	1298
97.76	97.62	- 0.14	443
97.74	97.77	0.03	1579

The development of an accurate calibration, *i.e.* determination of the 100 $^{\circ}$ Z point and dispersion of quartz in the near infra-red region, has facilitated the application of long wavelength polarimetry in sugar laboratories (Emmerich *et al.*, 1998 and Keitel, 1998). Subsequent collaborative testing of the proposed NIRPOL method for raw sugar, under the auspices of ICUMSA, have shown that the repeatabilities and reproducibilities are comparable with that of the conventional LAP method [GS 1/2/3-1] (Player *et al.*, 2000). These authors showed that the more coloured low pol sugar samples gave more repeatable results than the other sugars, proving that no difficulties are experienced as a result of sample colour.

Long wavelength polarimetric techniques have also been applied to factory products. Trott (1994) reported that stable and reproducible readings were obtained on dark solutions provided the turbidity is removed. Simpson and Corica (1997) investigated the use of a laser source operating in the near infra-red region at 830 nm. These authors compared the NIRPOL results with LAP results recorded at 830 nm and the conven-

tional 589 nm. Good agreement was obtained between the LAP results irrespective of the wavelength used to measure the rotation, while the NIRPOL samples treated with celite gave pol results that were 0.3°Z lower. Possible reasons for the observed differences are the subject of further investigation.

An automated juice analysis using NIRPOL measurements at 877 nm was developed by Crees and Brotherton (1990 and 1991) for factory control purposes. These authors found that during the 1989 season the NIRPOL results were on average 0.23% lower than the LAP results, while for the 1990 season the NIRPOL results were on average 0.12% higher than the LAP results. Paton and co-workers (1993) disproved previous theories that lead acetate preferentially precipitated levorotatory compounds such as fructose. Therefore, the observed increase in NIRPOL results could be attributed to the presence of dextran, since the latter is not removed through celite filtration and will inflate the NIRPOL readings. It is believed that the use of two different brix methods for calculating the NIRPOL and LAP results contributed to the observed differences in these pol results. King and Scroope (1998) implemented this automated system of juice analysis at Harwood mill. The results obtained between 1993 and 1997 indicate that excellent agreement was obtained between the NIRPOL and LAP results when the spindle brix result was used to calculate the pol% for both methods (Table 2). These authors propose that this method offers an effective alternative to the conventional LAP method and can be used for cane payment purposes.

Table 2. Results reported by King and Scroope (1998) for automated juice analysis.

Season	Number of samples	Difference in pol% juice NIRPOL - LAP
1993	1663	0.00 ± 0.21
1994	1628	-0.05 ± 0.21
1995	2042	-0.23 ± 0.24
1997	2146	-0.04 ± 0.13

The promising results reported here prompted the present investigation into the possibility of replacing the conventional LAP analysis of mixed juice with a long wavelength polarimetric technique. Although a comparison of the NIRPOL and LAP results is essential since cane payment has traditionally been based on the lead acetate pol results, the LAP method is not considered to be a suitable reference method since it is affected by the quantity of lead acetate used and the dextran levels of the sample (Simpson and Corica, 1997). Therefore, true sucrose (TSGC) determined by GC analysis was used as the reference method.

Procedure

The potential use of long wavelength polarimetry was evaluated on a comparative basis. The weekly composite mixed juice samples from four mills [Malelane (ML), Amatikulu (AK), Eston (ES) and Umzimkulu (UK)] representative of all the cane growing regions of South Africa, were used in this investigation. The samples were analysed in duplicate according to the NIRPOL method and the NIRPOL, LAP and TSGC analyses performed concurrently, thus eliminating the possibility of sample deterioration as a result of freezing and thawing. These NIRPOL results were compared with the weekly LAP and TSGC results used for cane payment.

In addition to the sample analysis a control sample was analysed in duplicate on a weekly basis. The control sample, a refinery 4th run-off, was sub-sampled and frozen at the beginning of the season. Ten of these frozen samples were thawed and analysed (diluted 4:1 so that they were representative of mixed juice) according to the NIRPOL and LAP methods to determine the control values for the 1999/2000 season.

The near infra-red polarimeter was calibrated to read at 882.6 nm according to the procedure outlined by Emmerich and co-workers (1998). The brix results used to calculate the pol% were measured on a Zeiss benchtop refractometer. All the pol readings were recorded on a 200 mm flow-through tube cooled to 20 ± 0.1°C.

The true sucrose analyses were performed routinely using the gas chromatographic method developed by Schaffler and Morel du Boil (1984).

Refractometric brix analysis of mixed juice [TM005] (Anon, 1996):

The juice (*ca.* 100 ml) is filtered through a filter paper (Postlip medium white w/s) containing celite 577 (*ca.* 1 g) and the funnel covered with a watch-glass to minimise evaporation. The first 25 - 30 ml of filtrate are run to waste until clear drops are observed and the clear filtrate is collected in a separate clean beaker for refractometric brix measurement. The brix value recorded at 20°C is used in the pol calculation.

Near infra-red polarisation method for mixed juice, without lead acetate clarification:

The juice sample (*ca.* 150 ml) was poured into a Schott bottle containing filter-cel grade celite (*ca.* 3.5 g), shaken and filtered (Schleicher and Schuell 3000 filter paper). The funnel was covered with a watch-glass during filtration to minimise evaporation. At least 15 ml of filtrate was run to waste and 50 - 60 ml of the clear filtrate collected in a separate clean beaker for the pol measurement at 882.6 nm.

The pol % juice is calculated from the polarimeter reading and brix measurement using the following equation:

$$\text{pol \%} = \frac{\alpha_R * 26}{d * 100} \quad (1)$$

Where: α_R = the measured polarisation
 d = the density of the solution determined from the brix reading

Mixed juice pol analysis [TM042] (Anon, 1996):

Basic lead acetate powder (*ca.* 1.5 g) was added to the juice in a 250 ml Schott bottle and the sample shaken vigorously to disperse the lead acetate completely. After allowing 30 s for flocculation, the sample was filtered (Schleicher and Schuell 3000). The funnel was covered with a watch-glass during filtration to minimise evaporation. The first 25 - 30 ml of filtrate was discarded and 50 - 60 ml of the clear filtrate collected in a separate clean beaker for the pol measurement at 589 nm.

The pol % juice is calculated using equation 1 above.

Results and Discussion

A comparison of the weekly NIRPOL, TSGC and LAP results illustrates the good agreement between these different methods of analysis for each of the mills studied (Figures 1a-d). To facilitate comparisons between the true sucrose and pol (apparent sucrose) results, the pol will be expressed as % sucrose for the purposes of this discussion.

The average differences in sucrose content, for weeks 13-31 of the 1999/2000 season, as a function of the method of analysis are recorded in Table 3. The mean difference between the NIRPOL and TSGC results, i.e. NIRPOL - TSGC, was $-0.06 \pm 0.07\%$ sucrose for the period studied, which does not constitute a statistically significant difference. Furthermore, this pol-true sucrose difference compares favourably with that between

Table 3. Comparison of the pol differences between the NIRPOL, LAP and TSGC methods.

Mill	AVG _{diff} ± SD (NIRPOL-TSGC)	AVG _{diff} ± SD (LAP-TSGC)	AVG _{diff} ± SD (NIRPOL-LAP)
ML	-0.12 ± 0.05	-0.1 ± 0.03	-0.02 ± 0.03
AK	-0.04 ± 0.07	-0.02 ± 0.06	-0.01 ± 0.04
ES	-0.01 ± 0.04	0.00 ± 0.04	-0.01 ± 0.03
UK	-0.05 ± 0.06	-0.04 ± 0.05	-0.01 ± 0.03
Overall	-0.06 ± 0.07	-0.04 ± 0.06	-0.01 ± 0.03

AVG_{diff} ± SD = average/mean difference ± standard deviation in the readings; NIRPOL = near infrared pol; TSGC = true sucrose by gas chromatography and LAP = lead acetate pol.

the LAP and TSGC results (LAP - TSGC), which gave a mean difference of $-0.04 \pm 0.06\%$ sucrose. The differences between the pol (NIRPOL and LAP) and true sucrose results could reasonably be attributed to experimental error, since the accepted tolerance for duplicate LAP analysis is 0.05% sucrose.

The average difference between these pol and true sucrose results for the mills studied are depicted in Figures 2 and 3. The larger difference between the NIRPOL-TSGC and LAP-TSGC

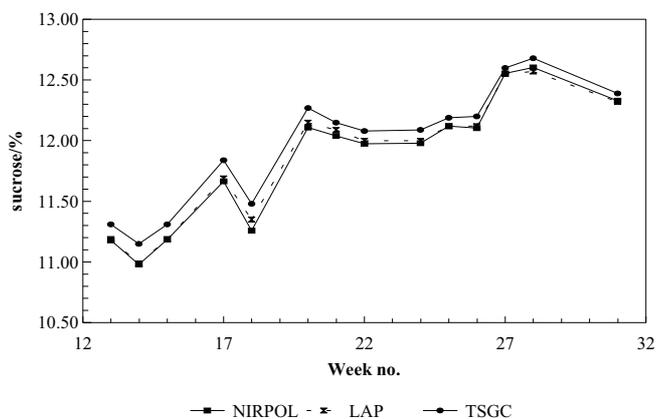


Figure 1a

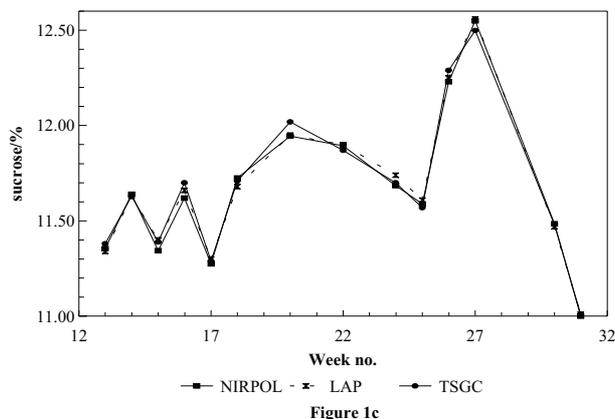


Figure 1c

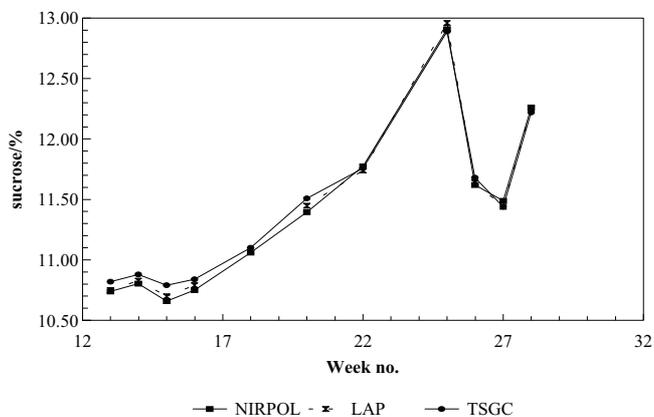


Figure 1b

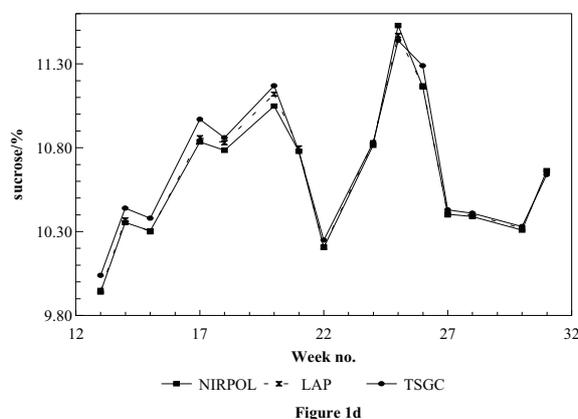


Figure 1d

Figure 1. Typical seasonal trends (weeks 13 - 31) for the mills studied.

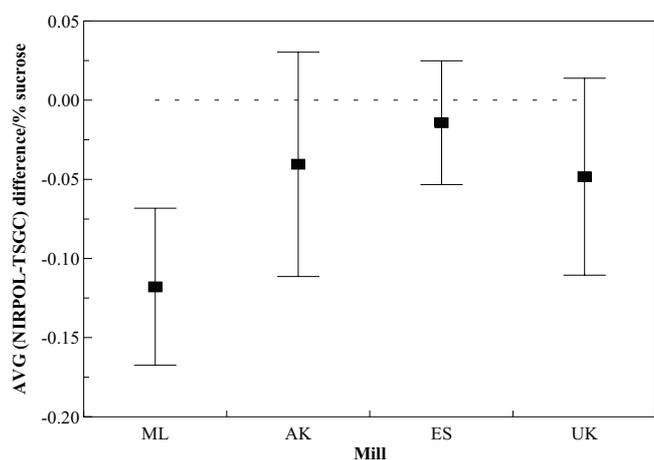


Figure 2. A comparison of the average NIRPOL-TSGC differences for the mills studied.

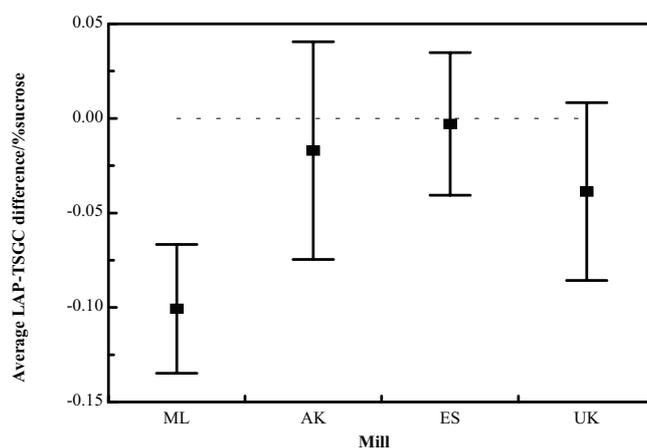


Figure 3. A comparison of the average LAP-TSGC differences for the mills studied.

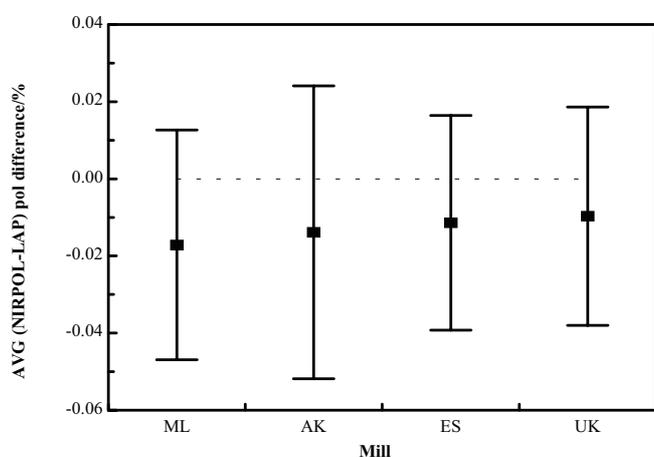


Figure 4. A comparison of the average NIRPOL-LAP differences for the mills studied.

results for Malelane (ML), compared with Eston (ES) could be attributed to many factors, e.g. cane handling procedures at the mill and/or the cane variety grown in a specific region.

Excellent agreement ($R^2 = 0.998$, $n = 54$) was observed between the NIRPOL and LAP results, with a mean difference (NIRPOL - LAP) of $-0.01 \pm 0.03\%$ sucrose for the mills studied (Figure 4).

Our results support the findings reported by King and Scroope (1998), which showed good agreement between the NIRPOL and LAP results for the 1993, 1994 and 1997 season (Table 2). The repeatability of the NIRPOL method (0.02% pol), calculated using the results of the duplicate analyses, is equivalent to that of the LAP method presently employed (Bissel, 1994).

A further consideration when proposing a change in the pol determination is the effect this method change will have on cane payment. The South African sugar industry uses the pol/

sucrose ratio, determined on a weekly basis at the Sugar Milling Research Institute (SMRI), to correct the pol readings recorded at the mill to a sucrose value for cane payment. Therefore, the absolute difference between the respective pol readings is inconsequential (Table 4), provided the pol results are representative of the true sucrose content, i.e. the same seasonal trend is followed (Figures 1a - d).

Conclusion

The NIRPOL method described here constitutes a suitable alternative to the conventional LAP analysis, based on the good agreement with both the TSGC and LAP results. In addition to eliminating the occupational health risks associated with the use/handling of lead acetate this methodology will also prevent the generation of large quantities of lead contaminated waste, which would in turn eliminate the costs incurred for the safe disposal of this hazardous waste. A further financial consideration is that the cost of basic lead acetate exceeds that of filter-cel grade celite. Therefore the use of the NIRPOL analysis constitutes a cost saving of R 0.60 per juice sample. Another advantage of the NIRPOL method is the simple sample preparation, which involves a single filtration step through filter-cel grade celite.

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Table 4. The effect of using the NIRPOL results on cane payment.

	Pol		True Sucrose	Pol/Sucrose ratio		Sucrose % for payment	
	NIRPOL	LAP		NIRPOL	LAP	NIRPOL	LAP
1	9.93	9.95	10.04	0.989	0.991	10.04	10.04
2	11.66	11.69	11.84	0.985	0.987	11.84	11.84

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