Sucrose content determination of sugar beet by NIR in an industrial context: network management and automation

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Introduction

In sugar beet factories, sucrose content is determined immediately on receipt of beet. In France, the procedure for sampling and analysingbeet is defined by lawand, since 1964, the official method for the determination of beet sucrose is a polarimetric measurement of beet juice that has been clarified using lead acetate. Several problems are raised by the use of lead acetate, which is a pollutant, as government regulation of the use of heavy metals becomes more and more stringent.

For the last four years, near infrared (NIR) spectroscopy has been studied as a suitable replacement for determining sugar content of beet. The aim of this study is to show, in an industrial context, the feasibility of replacing a polluting method by a non-polluting method such as NIR.

In the first part of this paper, the methods used in model development are described. In the second part, our approach to network management is presented. Finally, an automatic filling system (Foss-Parimix), developed in order to apply NIR in factories, is presented.

Materials and methods

Sugar beet origins and sample preparation

Sugar beets samples were collected from 15 sugar factories in different production areas of France. In each season from 1999 to 2002, samples of various qualities and varieties were collected several times from October to December. The protocol used for sample preparation was the standard method used in sugar factories. Twenty kilograms of beet were washed in order to remove residual traces of soil. The top of the beet was then removed and the root sampled using a multiple rasp to produce about 1 kg of fine brei (beet pulp). The sample was then homogenised with an approved mixer. To avoid changes in the samples due to oxidation and lost of moisture, the beet was analysed by NIRS immediately after sample preparation.

NIR spectral acquisition

A NIR reflectance spectrophotometer (Foss NIRSystems model 6500) with a large cup (Natural Product sample cup IH 0314P) containing 100 g of beet brei was used. Each spectrum (from 400 nm to 2498 nm at 2 nm intervals) was produced by averaging ten reference ceramic scans and 25 sample scans. Between samples, the cup was washed with distilled water at room temperature and dried. Immediately after the NIR measurement, the sugar content was determined by wet chemical analysis.

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Wet chemical analysis

All samples were analysed by our laboratory (Villeneuve d'Ascq, France). The sugar content was determined according to the ICUMSA official method adapted to French conditions. For each 26 g sample of sugar beet brei, 177 g (±0.20) of lead acetate solution was added and the solution blended for 5 min before being filtered through a filter paper. A polarisation measurement was then made on the clarified juice at a temperature of 20°C (±0.1).

Calibration and prediction on lab spectrometer

Software

WinISI (v1.04) software (developed by Infrasoft International) was used for spectral acquisition, data pre-treatment and model development.[6]

Data

Two samples sets were prepared, the first for calibration and other as a prediction set. The calibration set consisted of 2231 samples analysed from 1999 to 2001 and the validation set 525 samples analysed in 2001.

Modelling methods

Spectral pre-treatments, which correct the base line drift and the instrumental changes, were applied to the NIRS data. After a systematic study, the pre-treatments selected were SNV,De-trending (D)and second derivative (d2), with modified partial least squares (MPLS) as the regression method. The performance of prediction models was assessed using standard error of prediction corrected for bias [*SEP*(*C*)] and bias.

Network management

The main problems encountered with the network were that the calibration was not entirely stable over time and, when new instruments were introduced, the prediction error increased. The aim of this study is to have a low prediction error on three new slave instruments (Foss NIRSystems 6500).

Model update

In a previous report, we showed that the database should be updated at the beginning of each new campaign**.** The addition of 150 new samples was enough to take into account the beet variability from the new harvest.

Two different solutions were developed to solve the calibration transfer problem.

Robust model

The first was the construction of a robust model, which gave accurate predictions on several instruments. This was done by enriching the master instrument database (2231 samples) by adding 164, 70 and 99 slave spectra recorded on instruments 1, 2 and 3 respectively. A new model was then developed using the same pre-treatments as before.

Bias correction

The second solution was bias correction. Statistical tests suggested that slope correction was not necessary. A prediction model for sugar content was developed on the master instrument and predicted values for a set of 30 samples per slave instrument were used to calculate biases [Equation (1)]

$$\text{bias} = \bar{y}_{\text{ref}} - \bar{y}_{\text{NIR predicted}} \quad (1)$$

with $\bar{y}_{\text{ref}}$: mean concentration by wet chemical analysis, $\bar{y}_{\text{NIR predicted}}$: mean concentration predicted by NIR.

The equation $y_{\text{slave}} = \text{bias} + y_{\text{master}}$ computed from the standardisation set was applied to the validation set (y_{slave} is the sucrose values predicted with the slave instrument and y_{master} is the values predicted with the master instrument).

Automation

An automatic filling system was developed by Foss Tecator and Parimix (Figure 1). The monochromator (NIRSystems 6500) is sited horizontally beneath the automatic spreading system. With the current model, a sample is inserted manually into the bowl and the brei is spread automatically on the quartz window by a blade. After spreading, the bowl moves relative to the monochromator and the sample is scanned. When the spectrum is acquired, a trap door is opened and the sample is evacuated. The blade then removes any traces of brei and compressed air cleans the blade.

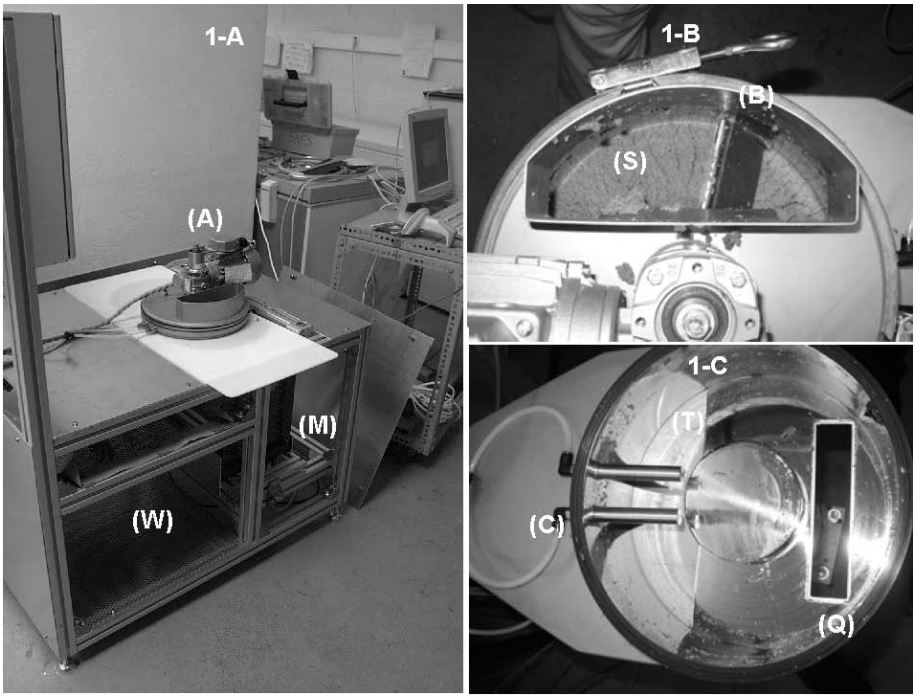

Figure 1. Automation of NIRS measurement. 1-A General view, 1-B External view of the automatic filling system, 1-C Internal view of the automatic filling system.
(A) Automatic filling system, (M) Monochromator, (W) Waste, (S) Sample, (B) Blade, (C) Compressed air, (Q) Quartz window, (T) Trap door.

Results and discussion

Model development

The aim of this study was to obtain accurate predictions of sugar concentration similar to those given by polarimetric measurement. Initially, systematic studies of the spectral pre-treatments, regression methods and spectral ranges were done in order to optimise the model, and MPLS regression with SNV+DT and second derivative (2:8:6) over the spectral range 1100 nm to 2498 nm was chosen (Figure 2).

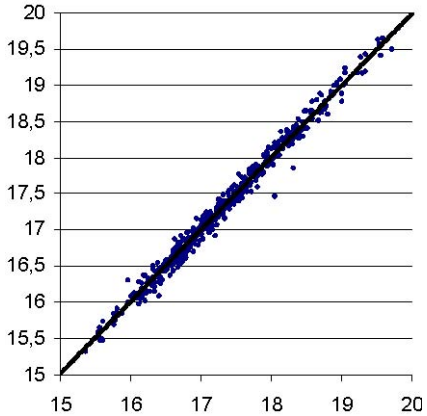

Figure 2. Validation on 525 samples. x-axis: lab values, y-axis: predicted values. *SEP* = 0.10 g/100 g fresh beet, *bias* = 0.003 g/100 g fresh beet, *R*= 0.989, *RPD* = 10.

Three parameters show the efficiency of the model:

- low values for *SEC* and *SEP* (0.09 and 0.11, respectively)
- a high correlation coefficient (*R*) between the reference and predicted values (R_{Cal} = 0.993 and R_{Val} = 0.989)
- An RPD (the ratio standard deviation/
- prediction error) of 10

From these figures, we can conclude that NIR is equivalent to the reference method. The samples were representative of the sugar beet population . The data set had a wide range of sucrose content (from 14 to 21 g/100 g of fresh weight) with a mean of 17.60 and a standard deviation (SD) of 1.1.

By using a large cup, the heterogeneity of the sample is taken into account and the repeatability of the NIR measurement is improved. The conclusion, therefore, is that sugar content of beet usually established by polarimetry can be predicted by NIR spectroscopy with low errors.

Instrument network management

The main results are summarized in Table1. The two solutions described earlier relating to the management of several instruments give accurate results. The development of a robust model permits us to obtain a low bias and a low *SEP* for all the slave instruments while bias correction is a simple solution but accurate.

In practice, the spectra database will be managed as follows:

- variability of beet from the new harvest is handled by adding 150 samples from each new campaign to the main database
- instrument variability is handled by the analysis of 150 samples per instrument and the development of a robust model

Table 1. Two solutions to the calibration transfer problem—*SEP* (g/100 g of beet) for each instrument with different models.

	Instrument 1	Instrument 2	Instrument 3
Master model	0.17	0.17	0.62
Master model with bias correction	0.12	0.11	0.16
Multi-instrument model	0.09	0.11	0.14

Automation

Validation of the model developed using the master laboratory system with a data set of 662 samples gave a high SEP (0.25 g/100 g) due to a high bias (–0.21). However, a model developed with spectra data base containing 2360 spectra analysed with the manual system and 1046 spectra recorded with the automatic system give a low bias on the four instruments (Table2). It is important to notice that spectra analysed on the lab system can be used to develop an automatic model. In this way, we keep the variability of four years of data in our study.

Cross-contamination between samples does not seem to be a problem: cleaning between samples is sufficient. The prototype will be further developed by Foss Tecator and, for industrial use, we hope to automate the sample introduction to have a full automatic system.

Table 2. Validation with four automatic instruments – (unit : g/100 g of beet).

	Instrument I	Instrument II	Instrument III	Instrument IV
No. samples	662	686	352	404
Bias	–0.01	0.03	0.00	0.06
SEP(*C*)	0.12	0.11	0.13	0.13

Conclusions

This study shows the feasibility of NIR spectroscopy to determine sugar content of sugar beet brei. Initially, several spectral pre-processing and regression methods were tested in order to produce an accurate prediction of sugar content. A model, using SNV and second derivative, gave the most accurate results on a validation set of 525 samples. The standard error of prediction was 0.10 g of sucrose/100 g of fresh beet over a large concentration range (14–21 g/100 g), an accuracy suitable for sucrose prediction.

For industrial use, the spectral database could be updated by the addition of a few samples (150) to maintain a low *SEP*. The transfer of this calibration was then studied and the solution adopted was a robust model developed by using a calibration set containing spectra from several instruments. In conclusion, prediction of the polarimetric measurement using several NIR instruments is feasible in an industrial context. Finally, automation of NIR measurements using an automatic filling system coupled to a spectrometer was developed and accurate results obtained.

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