# Possibilities of milk analysis on ZX 100C NIT Instrument

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## Introduction

Zeltex Inc. Hagerstown, USA is a well-known producer of portable NIT analyzers. Our company, MILL TECH Export/Import Ltd, Hungary is a widely distributor of Zeltex's NIR equipment in Europe, with a lot of experience in applications of this type of instruments (together with appropriate calibrations). ZX 100C is one of Zeltex's earliest portable analyzers and it was intended widely to use in food industry: for analysing grains and cereals, food and beverages of different density (liquid, pasty, slurries). Light source is an array of 14 diodes equipped with appropriate filters; sample chamber suitable for holding sample cuvettes of different size; a light shield with termistor inside it to measure sample temperature can be connected to the instrument. When measuring, the basic light energy is detected at the first and the last measurement, usually with empty chamber. The instrument uses linear calibration based on optics data in AU, there is no data pre-treatment (transformation, derivatives). In this paper, the results of the process realizing potential application opportunities 'built-in' the instrument for different products and their constituents are presented. In this case, the realizing process, which has taken market expectance into consideration, means that calibrations have been developed and verified, and the accuracy and other statistics of the calibrations obtained have been assessed. The results can hopefully demonstrate applicability of instruments with similar feature and similar operation base, what's more, calibration constants obtained could be used with some adjustment on the similar instruments.

### Beginning….

First, ZX 100C was tested for analyses of wheat protein, moisture (instrument was pre-calibrated for protein and moisture using American varieties of wheat but not Hungarian ones) and as analyses of wheat gluten is Hungarian (and Central European) speciality, a calibration for gluten was developed. The results were promising but not satisfactory enough due to small number of samples and special characteristics of gluten. As Zeltex Inc. soon entered the market with an instrument,ZX50 definitely more suitable for analysing grains, we tried to find other applications for ZX 100C. We started to develop calibrations for raw milk because there seemed to be a real market demand and results and conclusions could be transferred to other diary products, too. First, development of calibrations was focused on major components of raw milk: fat, protein, lactose and solid material. First calibrations were made by running 40 sample at temperatures of about 40 $^{o}$C.

### … and continuation

In the domestic market of Hungary, composition of raw milk is important factor, even more important, however, is to test whether milk biologically uninfected, pure, and genuine, that is to analyse these characteristics such as somatic cell, freezing point (as indicator of 'not original water content') by NIT. Our aim became testing how to measure these parameters and how well.



Near Infrared Spectroscopy: Proceedings of the 11th International Conference.

## Samples and measurements

**Table 1. Summary of the independent sample sets**

| | I | II | III |
|---|---|---|---|
| Number of samples | 27 | 32 | 15 |
| Sample temperature (°C) | 18-22 | 20-30 | 30 |
| Temperature of instrument(°C) | 18-22 | 18-22 | 20-22 |

Milk samples need specially careful handling when collected, measured with reference method. Not simple case. But we were lucky, as sample amount of 10 ml is enough for one measurement. This amount is so small that we could use the rest of samples of a lab which was analysed and judged for pouring out (I. and II sample sets). Sample set III is composed of raw milk of 3 different origins, adding different amounts of water to each. Measurements were made at different temperatures so that dependence of sample temperature was taken into account. Distribution of not all constituents in sample set I and II: are the best The samples were not selected ones. **Calibration Data** were composed of sample set I and some part of set II,. **Validation Data** were the rest of sample set II. On calculating freezing point, sample set III was added to Calibration Data.

## Procedures and programs used in evaluation

Two problems had to be taken into consideration in calculation of calibration constants. On one hand the number of sample is small, and distributions of constituents are not optimal. So we tried to select the more suitable procedure below for computing calibration constants.

**MLR** calibration software supplied with the instrument was used for calculating constants and for prediction of Validation Data.

**OWLS** program was used, in the case of few samples, so that not all the filters but a few best filters should be involved in calibration. The combination of filters has been accepted that good enough statistics were obtained for on Calibration Data and simultaneously, acceptable statistical figures on independent Validation Data were resulted in without practically changing bias and slope.

**PLS1** method was used, besides the case of few samples, when more accurate calibration was expected by eliminating intercorrelation, and all the wavelengths were supposed to be involved in the estimation of a particular constituent.

## Measuring components of raw milk

The developed first constants were checked on Sample Set I. Only for fat were the results obtained acceptable without hesitation. For the rest of components, better established and more accurate results were expected from new calibration constants. The new calibration constants were calculated on Calibration Data then validated on the independent Validation Data.

**Table 2. The main statistical figures characterising calibrations.**

| | Fat (%) | Protein (%) | Lactose (%) | S.N.F (%) | -FP (°C) | Somatic cells |
|---|---|---|---|---|---|---|
| Range of Calibration | - | 2,9-4,2 | 3,8-5,3 | 8,4-10,5 | 0,488-0,546 | 61-870(*1000) |
| Corr.Coeff. Of Cal. | - | 0,92 | 0,68 | 0,84 | 0,91 | 0,87 |
| SEE | - | 0,11 | ~0,2 | <0,3 | 0,0066 | 96*1000 |
| Range of Validation | 3,0-5,5 | 3,4-4,2 | 3,8-5,3 | 9,2-10,4 | 0,531-0,541 | |
| Corr.Coeff. Of Val. | 0,98 | 0,77 | 0,68 | 0,6 | - | |
| SEP | 0,1 | -0,15 | <0,2 | <0,25 | ~0,01 | |

### Fat

On prediction of Sample Set I, the calibration constants resulted in good accuracy without changing bias an slope. (In Figure 1, the goodness of prediction can be illustrated.)

### Protein

Result of protein calibration is acceptable as is seen in **Figure 2.**

### Lactose

Lactose can be measured, although the statistical figures are not convincing. This is because the real range of lactose values is very narrow. This is not optimal concerning calibration, either. Figure 3 illustrates how well fitting has been succeded in.

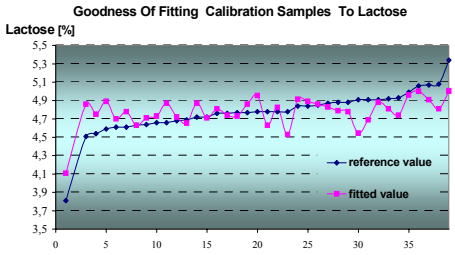


**Figure 1**

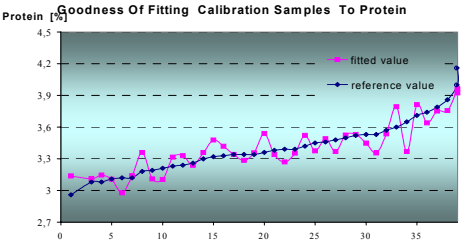


**Figure 2**

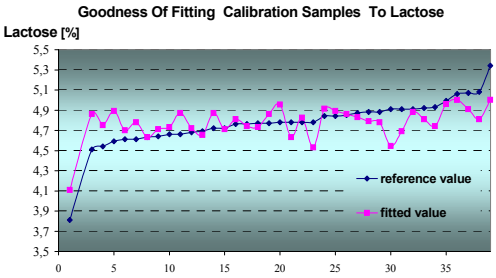


**Figure 3**

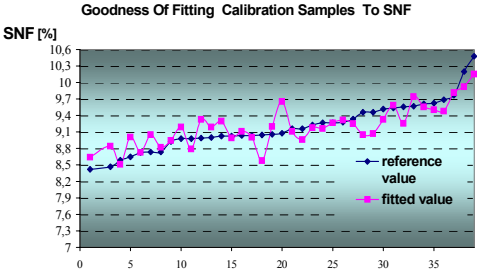


**Figure 4**

### S.N.F.

Snf values can be measured ,too. Its distribution is similar to those of lactose. And remember, solids are minerals and these do not have absorbance at infrared wavelengths. In **Figure 4**, goodness of fitting can be illustrated.

## Measuring freezing point of raw milk

The distribution of FP in Calibration Data was improved with addition of Sample Set III and elimination a few samples of very frequent value. Validation Data remained unchanged. Two methods were used: **OWLS** program without validation file and PLS1. Both calculations gave results with similar accuracy. Using PLS1, to choose the optimal number of PLS1 factors, we used the Validation Data for extra prediction. 12 factors gave the best result. Because Validation Data

cover a very narrow range for FP, just one figure (SEP) makes sense statistically. As SEE is 0,01 °C, FP can only be predicted with accuracy of more than 0,01 °C. This is not enough for a good measurement. But calibration is

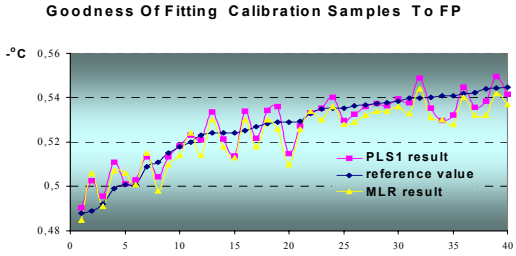


Fig.5

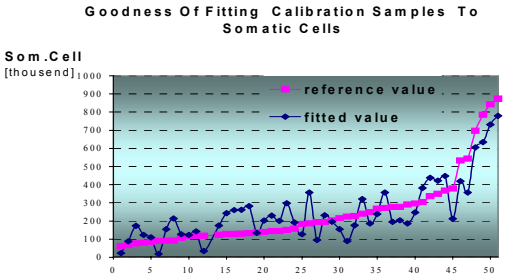


Fig.6

usable to deciding whether water content meet standard. In Hungary, FP generally falls in the range of -0,525 to -0,540 and its limit -0,520.

## Measuring somatic cell in raw milk

We combined I and II Sample Sets to have a bigger calibration set for a more robust calibration and eliminated several outlier samples. Sorry, so there have not remained any samples for validation. This is a task left for later. PLS1 method was used for evaluation to eliminate the intercorrelations..12 PLS factors were accepted. The goodness of calibration is illustrated in **Figure 6**. The fact that the magnitude of the error is so big means the prediction of somatic cell only gives qualifying/ classifying information and not a real measured value.

## Conclusion

The results, as expected, show the organic substances (fat, lactose, protein) that directly affect absorbance at particular wavelengths of ZX 100C can be measured satisfactorily, solid material (such as minerals) relatively well measured due to correlation between solid content and organic composition of raw milk and/or it makes a slight modification on spectrum.

The parameters, such as freezing point, somatic cell which does not have any specific absorbance wavelengths can not be measured with the same accuracy as minerals and organic substances, but despite this fact, their analyses can be useful for some practical fields (with FP, for testing overstep the upper limit of standard, with somatic cell, for classifying).

The instrument, with the accuracy obtained (and its reasonable price) seems to get useful for milk-producing farmers and collectors of Raw milk to handle and collect milk considering economical point of view. The calibrations developed suggest that other diary products (commercial milk, yoghurt,..) could be measured. The new developed ZX 550 can be calibrated for raw milk by fewer samples than anyway using the calibration constants of ZX 100C.