



Evaluation of benchtop versus portable near-infrared spectroscopic method combined with multivariate approaches for the fast and simultaneous quantitative analysis of main sugars in syrup formulations



Raphael Henn, Anita Schwab, Christian W. Huck*

Institute of Analytical Chemistry and Radiochemistry, CCB-Center for Chemistry and Biomedicine, Leopold Franzens University, Innsrain 80/82, 6020 Innsbruck, Austria

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ABSTRACT

In this work a total of 116 syrup samples was investigated in order to establish predictive models for glucose, fructose and sucrose of sufficient accuracy based on partial least squares regression. The samples are divided into two main groups a) standard syrups b) reformulated syrups. The latter products can be distinguished via the very low amount of glucose and sucrose and a high amount of fructose which makes them suitable for special nutrition. Near-infrared spectroscopy was applied together with Multivariate Analysis to develop a new method for quality control of syrups. Comparison between a portable spectrometer and the benchtop device showed that the reduced wavelength range and reduced resolution of the portable device is sufficient to receive calibrations with $R^2 \geq 0.96$ for standard syrups with comparable SEP values of 1.30 g/100 g vs. 1.19 g/100 g, 0.94 g/100 g vs. 0.99 g/100 g and 2.04 g/100 g vs. 2.46 g/100 g for glucose, fructose and sucrose respectively using the handheld device. The SEP values led to high RPD values of 5.56 vs. 5.26, 4.30 vs. 4.72, 5.06 vs. 4.20 for fructose, glucose and sucrose respectively. The R^2 values for reformulated syrups were 0.94 with a SEP of 1.04 g/100 g and a RPD value of 2.58 for the portable spectrometer and 0.92 with a SEP of 0.92 g/100 g and a resulting RPD value of 2.84 for the benchtop spectrometer. The method is suitable to be implemented for quality control in the producing industry as well as in grocery stores.

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1. Introduction

Near-infrared spectroscopy (NIRS) is an analytical technology exploiting the interaction between light and matter to gain information on properties and ingredients, which offers some advantages in comparison to classical chemical analysis like liquid chromatography, gas chromatography or mass spectrometry. In most cases NIRS does not require sample preparation, is nondestructive, easy to handle and gives access to multiple chemical as well as physical properties at the same time (Tsuchikawa, 2007). Furthermore it is cheap and easy to automatize. NIR technology offers even more key advantages such as usage of optical fibers (Siesler, Ozaki, Kawata, & Heise, 2008) and the abandonment of

possibly toxic chemicals and a very low effort of energy which makes it real “green science” (Schmutzler, Beganovic, Böhler, & Huck, 2015). Despite all, the drawbacks are: establishing a suitable calibration is a lot of effort and requires reference values for each sample, which makes it time consuming and costly at the beginning (Bakeev, 2010).

NIRS is concerned with both electronic and vibrational transitions (Ozaki, 2012). Bands due to electronic transitions observed in the NIR region are, in general, weak. Moreover, bands arising from overtones and combination modes are so-called forbidden transitions. The NIR region may be divided into region I (12,500–8500 cm^{-1}), region II (8500–5500 cm^{-1}) and region III (5500–4000 cm^{-1}) (Siesler et al., 2008) whereas the borders of the three regions are not rigorous. Region I is known as “the short wave NIR (SWNIR) region”, “near NIR (NNIR) region”, or “the Herschel region”. In this energetic range, bands due to electronic transitions and those due to overtones and combination modes can be

* Corresponding author.

E-mail addresses: Raphael.henn@uibk.ac.at (R. Henn), anita.schwab@student.uibk.ac.at (A. Schwab), Christian.W.Huck@uibk.ac.at (C.W. Huck).

observed. All of the bands appearing in this spectral region are very weak. Therefore this energetic range shows a high transparency and is called “the window of body”, which is being used for biomedical applications frequently (Petter et al., 2009). In region II, bands arising from the first overtones of XH (X = C, O, N) stretching vibrations and various types of combination modes of XH vibrations occur. Region III is a combination mode region. The permeability of region III is comparatively poorer. Many applications use regions II and III (Ozaki, 2012).

NIRS can be applied to a wide variety of problems such as determination of particle size (Bittner et al., 2011), determination of the best time of harvesting (Huck, 2015), investigation of the geographical origin of food such as apples, meat, cheese (Huck-Pezzei et al., 2014) or predicting the amount of glucosinolate in rapeseeds (Pierna et al., 2011). Also the determination of individual sugars in aqueous solutions and fruit juices as well as structural studies dealing with the distortions of water clusters can be achieved via NIRS (Giangiaco, 2006; Giangiaco & Dull, 1986; Rambla, Garrigues, & delaGuardia, 1997; Rodriguez-Saona, Fry, McLaughlin, & Calvey, 2001). Generally speaking NIRS is a versatile technology covering polymer chemistry, measurement of blood glucose, monitoring of calcination reactions and many more as it can be read throughout the literature (Ozaki, 2012).

After recent scandals in food industry such as the horse meat scandal (European-Commission, 2013) the calling for more detailed examination of food, in general, is getting louder which results in the demand for novel quick and cheap analysis methods. This task could be accomplished by NIRS in many areas. The applied technology can be easily automated and offers the possibility for real time monitoring of processes (on- and inline). This feature makes it possible to optimize a process in a much more specific way instead of evaluating just the final product in special laboratories (offline). These measurements take a lot of time, which could be in the order of hours, in which a great amount of poor quality product may have already been produced (Coates et al., 2003).

Due to the fact that syrup does play a big role in juice industry in general, since the reduced weight offers the potential of huge savings when it comes to transport costs there is a need for novel technologies which can deal with a big amount of samples in a very short time with high accuracy. This gets even clearer because the typically used method for the determination of sugar content is the enzymatic hydrolysis of the individual sugars (Steegmans, Iliens, & Hoebregs, 2004) or HPLC with refractive index detector (Zielinski et al., 2014) which both take their time.

The objective of the present study was the establishment of a portable NIR spectrometer for the quantitative determination of glucose, fructose and sucrose in syrup and the comparison of the prediction accuracy with the bench top spectrometer.

2. Materials and methods

Recent developments of miniaturized spectrometers offer a wide field of applications which makes it possible to take measurements at any place and to get immediate results without time consuming transportation and analysis processes (Zamora-Rojas, Perez-Marin, De Pedro-Sanz, Guerrero-Ginel, & Garrido-Varo, 2012). In this study NIRS was applied to two different kinds of syrups, namely standard syrups and reformulated (further on referred to as Reform) syrups which differ strongly in their carbohydrate composition as can be seen in Fig. 1. Two differently designed spectrometers were applied to syrup samples in order to compare the performance of a portable device with that of a benchtop spectrometer. Those spectrometers differ not only in size, but also in terms of resolution, the accessible wavelength range and the built in technology. The usage of the portable spectrometer

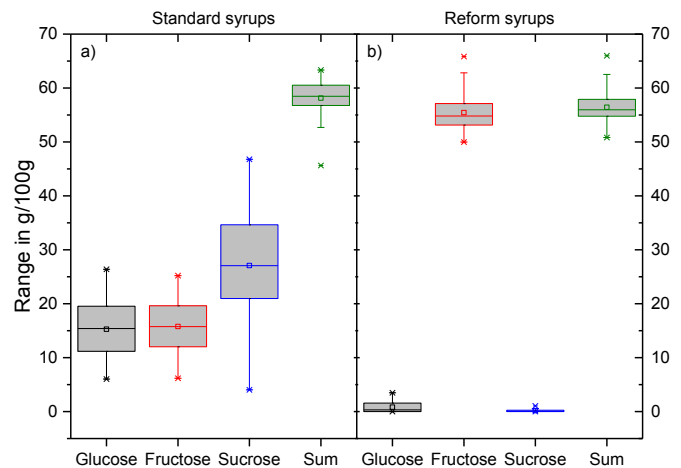


Fig. 1. Carbohydrate distribution for standard (a) and Reform (b) syrups.

comes with several advantages such as great flexibility and easy application but along comes the lack of high end performance, resolution and individualizations. The combination of NIRS and Multivariate Analysis (MVA) provides a powerful tool which makes it possible to identify the amount of all three main sugars (sucrose, fructose and glucose) in standard syrups within just a few seconds. While investigating Reform syrups the focus was put on measuring the sum of glucose and sucrose in order to monitor the observance of the limit of a maximum of 5 g/100 g to provide a powerful tool for the quality control of syrups which are suitable for people who must avoid the uptake of greater amounts of glucose and sucrose. The main objective of the investigated product is its use as a drink which is being made via dilution of the actual product with water.

2.1. Samples

A total of 116 samples was investigated, those can be divided into 63 Reform and 53 standard syrup samples. These samples were provided by our industrial partner and were stored at -20°C before and after the measurements. There was a variety of 13 different tastes (sour cherry, pomegranate, blueberry, peach-maracuya, orange-passion fruit, melissa, elderflower, black elder, raspberry, black currant, wild cranberry, strawberry-lime-melissa, strawberry-lime). Reform syrups contained only three different kinds of taste namely elderflower, black currant and raspberry while the standard ones contain all of the listed different tastes. The composition of the main carbohydrates in entirety is being illustrated in Fig. 1. As one can see the amount of glucose and sucrose in Reform syrups is below 3.48% and 1.06% respectively, so the samples were spiked (added sugar was dissolved in water bath 5 h at 90°C) in order to get a wider range of concentrations to apply Partial Least Squares Regression (PLSR) and exceed the limit which is checked for. The added carbohydrates (D-(+)-Glucose and D-(+)-Sucrose) were purchased from Sigma Aldrich (purity level of $\geq 99.5\%$). The resulting concentrations reached from 0 to 8 g/100 g for glucose, 0–7 g/100 g sucrose which led to a range of 0–10 g/100 g in their corresponding sum. This procedure was not found to be necessary with standard syrups, since the variation in the main sugar composition was high enough. The mean and standard deviation values for standard syrups were 15.27 ± 5.43 g/100 g, 15.77 ± 5.10 g/100 g, 27.08 ± 10.60 g/100 g and 58.13 ± 3.38 g/100 g for glucose, fructose, sucrose and the resulting sum respectively. The composition of reform syrups was 0.82 ± 0.86 g/100 g, 55.43 ± 3.09 g/100 g, 0.18 ± 0.26 g/100 g and 56.43 ± 2.85 g/100 g

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