Quantitative and qualitative differentiations of alcoholic beverages by near infrared spectroscopy

Szilveszter Gergely, Krisztina Farkas, Andrea Forgács and András Salgó

Department of Biochemistry and Food Technology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary. gergely@mail.bme.hu

Introduction

Manufacturers of alcoholic beverages are keen to introduce quality control methods that enable them to measure the composition of their products on a quasi-continuous basis. Analytical methods to be applied in this way need to meet two requirements: (1) measurement of chemical composition[1] (and colour),[1,2] (2) determination of authenticity (origin) or adulteration, falsification, imitation *etc.* of materials tested.[3,4] Over the past ten years feasibility studies have been carried out to ascertain the suitability of near infrared spectroscopy for this purpose.[5–8]

The aim of this study was to investigate the near infrared (NIR) spectra of alcoholic beverages with a view to extracting the hidden information they contain and using it for quality grading of products.

Materials and methods

118 samples of different types of liqueur and vermouth, 96 of different types of wine and 23 of different types of champagne were investigated. Liqueur and vermouth samples were scanned in transmission mode from 1000 to 2500 nm with Rapitec 5665 with fibre optic (3 mm optical path length), the wine and champagne samples were scanned in the same wavelength region with NIRSystems 6500 fitted with a sample transport module (1, 4 and 10 mm quartz cuvette) (Foss-NIRSystems, Silver Spring, MD, USA). Data were collected every 2 nm (700 data points per spectrum) and the raw spectra were transformed into second derivatives (D2OD) using a 10 nm segment and 0 nm gap size.

Partial least squares (PLS) calibrations were developed for determining the alcohol, extract, invert sugar, citric acid, sulphurous acid, iron, copper content of wine samples and the alcohol, reducing sugar, sulphurous acid content of champagne samples. The optimum number of PLS factors used in a model was determine by a cross-validation procedure with four segments.

In the polar qualification system (PQS),[9] the D2OD spectrum is plotted in a polar coordinate system on a two-dimensional quality plane and the centre of gravity of the spectrum is given as a point, known as the quality point. In the PQS, the length of the vector is a function of the size of the spectral value, while the angle is a function of the wavelength.

Spectral and reference data were processed using NIRSystems Spectral Analysis Software (NSAS), Ver. 3.30 and with PQS32 Evaluation Software, Ver. 1.37 (Metrika R&D Co., Budapest, Hungary) respectively.

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

Results and discussion

Quantitative differentiations

Both raw and second derivative spectra were handled by PLS calibrations. Truncated wavelength region was used in case of spectra collected with 4 and 10 mm cuvettes to eliminate noisy regions when log(1/*R*) spectra value show higher, than three absorbance units (Figure 1).

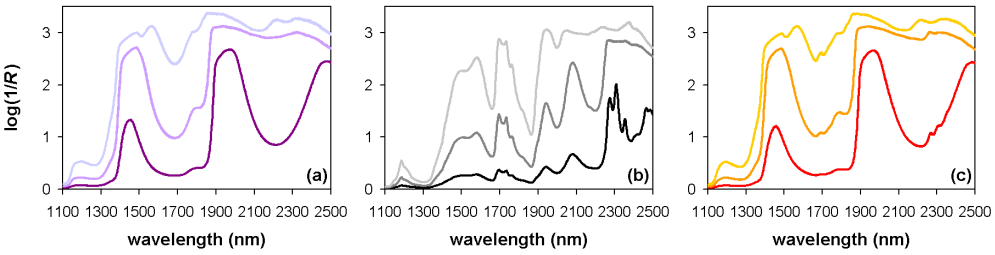

Figure 1. Log(1/*R*) spectra of (a) water, (b) ethanol and (c) wine using cuvettes with different pathlength (upwards from below: dark colour = 1 mm, medium colour = 4 mm, light colour = 10 mm).

The PLS results show small differences using 1 and 4 mm cuvette in 1100–2500 and 1100–1870 nm region respectively. In case of champagnes the main advantage of 1 mm cuvette was the "anti-bubble" effect causing by small thickness. The main constituents (concentration > 5 g l^{-1}) can be predicted with an acceptable accuracy (Figure 2).

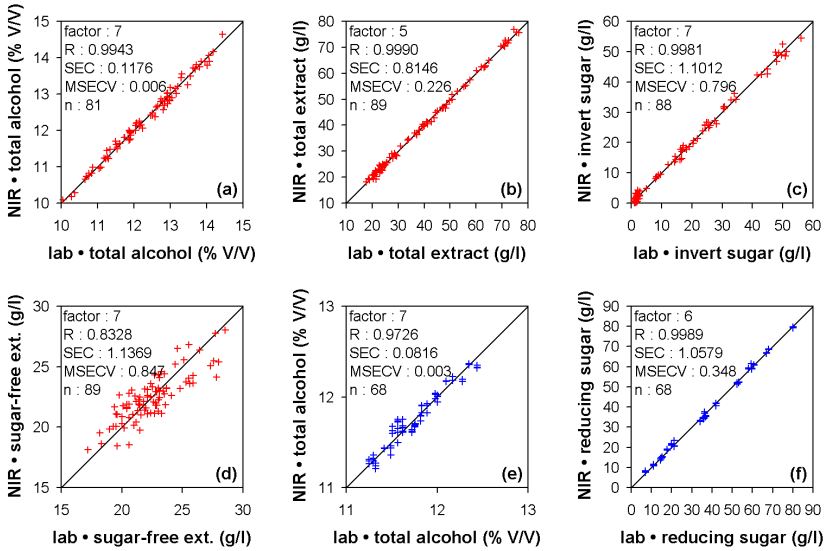

Figure 2. Scatter plot of (a) total alcohol, (b) total extract, (c) invert sugar, (d) sugar-free extract of wine and (e) total alcohol, (f) reducing sugar of champagne. The constituent values are predicted by PLS (1100–2500 nm) using log(1/*R*) spectra collected in 1 mm cuvette.

Qualitative differentiations

PQS methodology was used to extract hidden information from the NIR spectra, the most "sensitive" regions of second derivative spectra being selected based on spectral variability. Using these regions, the quality points of the samples were then drawn in the quality plane.

In case of liqueurs and vermouths the greatest variable was the change in the alcohol and extract content of the samples tested (Figure 3).

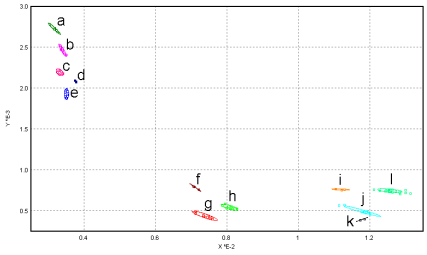

Figure 3. Quality points of liqueur and vermouth samples using the 1140–1230 nm range of second derivative spectra (line method, non-selected points are omitted). Alcohol and extract content of samples a = 18%, 26 g l^{-1}; b = 17.5%, 75 g l^{-1}; c = 16%, 150 g l^{-1}; d = 17.5%, 150 g l^{-1}; e = 16%, 180 g l^{-1}; f = 25%, 250 g l^{-1}; g = 25%, 330 g l^{-1}; h = 27%, 280 g l^{-1}; i = 37%, 180 g l^{-1}; j = 36%, 230 g l^{-1}; k = 38%, 300 g l^{-1}; l = 40%, 175 g l^{-1} respectively.

The differentiation between wine and champagne samples was developed for invert sugar content (Figure 4).

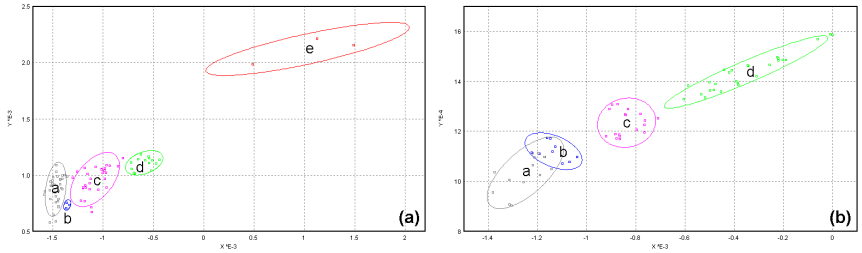

Figure 4. Quality points of (a) wine samples (a = dry; b = medium dry; c = medium sweet; d = sweet; e = "aszú" wines) and (b) champagne samples (a = extra dry and brut; b = dry; c = medium dry; d = sweet champagnes) using the 2060–2150 nm range of second derivative spectra (line method, non-selected points are omitted).

Conclusion

The NIR measurements of alcoholic beverages were optimized in a 1 mm cuvette in transmission mode. The main constituents were assigned correctly in all types of beverages: alcohol, extract, invert sugar and reducing sugar contents were predicted with high accuracy. Results indicate that the transmission spectra of alcoholic beverages reveal additional information about product quality that can be extracted with the help of PQS. The different product groups were clearly segregated, and there was no (or small) overlap between similar products. The basis of differentiations is the absorption bands of sugar and/or alcohol detected sensitively in transmission spectra.

References

1. R. Vonach, B. Lendl and R. Kellner, *J. Chromatogr. A* **824,** 159 (1998).
2. S. Pérez-Magariño and M.L. González-Sanjosé, *Food Chem.* **81,** 301 (2003).
3. M. Palma and C.G. Barroso, *Talanta* **58,** 265 (2002).
4. C.M. Almeida and M.T.S.D. Vasconcelos, *J. Anal. At. Spectrom.* **16,** 607 (2001).
5. L. Sauvage, D. Frank, J. Stearne and M.B. Millikan, *Anal. Chim. Acta* **458,** 223 (2002).
6. R.G. Dambergs, A. Kambouris, I.L. Francis and M. Gishen, *J. Agric. Food Chem.* **50,** 3079 (2002).
7. C.M. Garcia-Jares and B. Médina, *Fresenius J. Anal. Chem.* **357,** 86 (1997).
8. R. Medrano, S.H. Yan, M. Maudoux, V. Baeten and M. Meurens, in *Leaping Ahead with Near Infrared Spectroscopy*, Ed by G.D. Batten, P.C. Flinn, L.A. Welsh and A.B. Blakeney. Royal Australian Chemical Institute, Victoria, Australia, p. 303 (1995).
9. K.J. Kaffka and L.S. Gyarmati, *J. Near Infrared Spectrosc.* **6,** A191 (1998).