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Food authentication—has near infrared spectroscopy a role?

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Introduction

Globalisation is hailed by many pundits as one of the great economic milestones in the development of world economies. The food industry has been affected by this trend as much as any other. Demand for a broad range of foodstuffs from faraway places has arisen from the increased economic wealth of the Western consumer and the greater opportunities for foreign travel that we all now enjoy. One of the dangers inherent in such trade lies in the opportunity that arises for economic fraud on account of the considerable physical separation of producer and consumer. Such fraud may involve the adulteration of a foodstuff or the falsification of added-value claims, e.g. geographic origin. The food processing industry needs analytical tools to verify the nature of high-value foods in particular in order to protect their brands; ideally, these tools should permit rapid, non-destructive and inexpensive analysis at any point in the distribution chain. Near infrared (NIR) spectroscopy has the potential to meet these requirements and this article reports aspects of some recent investigations into food adulteration problems.

Example 1: honey adulteration

Honey is a high-value foodstuff which is believed to be a target for adulteration. Given its composition (typically 80% carbohydrate and 17% water), this would most simply take the form of extension by cheaper, commercially-available sugar syrups. In a recent feasibility study,[1] the ability of NIR spectroscopy to detect adulteration of Irish artisanal honeys by either added beet invert (BI) syrup or high fructose corn syrup (HFCS) was studied.

Honey samples (n=83) were obtained directly from beekeepers throughout the island of Ireland. Adulterant solutions comprised fully-inverted beet syrup (50:50 fructose:glucose) and high fructose corn syrup (45% fructose and 55% glucose). A number (n=18) of authentic honeys were chosen at random; eight were each adulterated with beet invert sugar at levels of 7, 10, 14, 21, 30, 50 and 70% w/w, while high fructose corn syrup was added to the remaining 10 authentic honeys at 10, 30, 50 and 70% w/w. This produced 56 BI-adulterated and 40 HFCS-adulterated samples. Samples were standardised to 70°Brix, placed in a camlock transflectance cell fitted with a gold-plated reflector (0.1 mm sample thickness) and scanned between 1100 and 2498 nm using a NIRSystems 6500 scanning monochromator (Foss NIRSystems, Silver Springs, MD, USA) equipped with a sample transport module. Spectral data were recorded as log 1/T (T=transflectance) using WINISI software (version 1.04a; Infrasoft International, Port Matilda, MD, USA). Raw and 2nd derivative spectra (10 nm gap and segment size) of typical samples are shown in Figure 1(a) and 1(b).

Raw spectra are dominated by peaks at 1490, 1945, 2120, 2298 and 2490 nm; the only evidence of difference lies in small variations in amplitude below

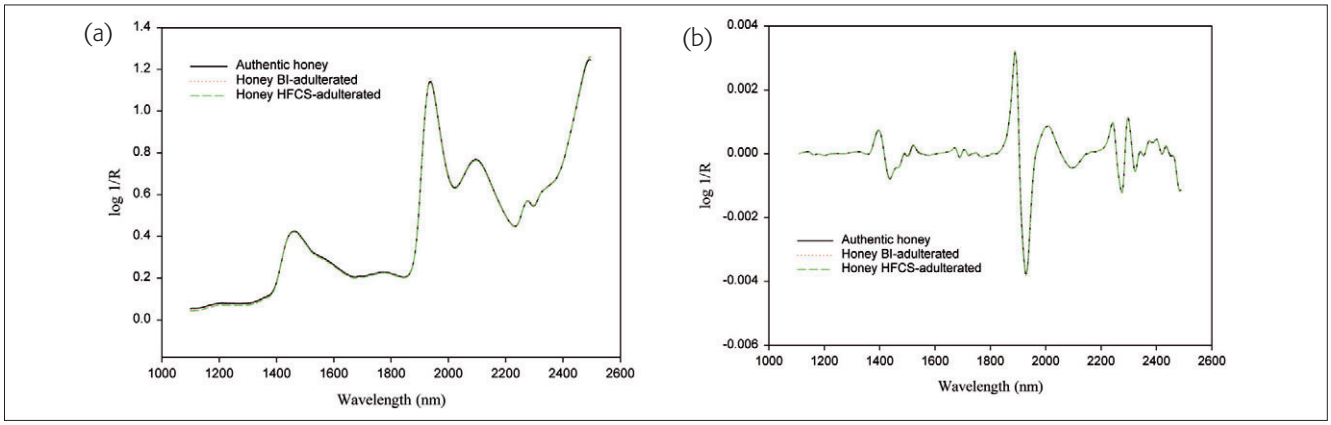

Figure 1. Overlaid raw (a) and 2nd derivative (b) transflectance spectra of a randomly selected authentic honey and the same honey adulterated with beet invert (70% w/w) and high fructose corn syrup (70% w/w). (Reproduced by permission of NIR Publications.)

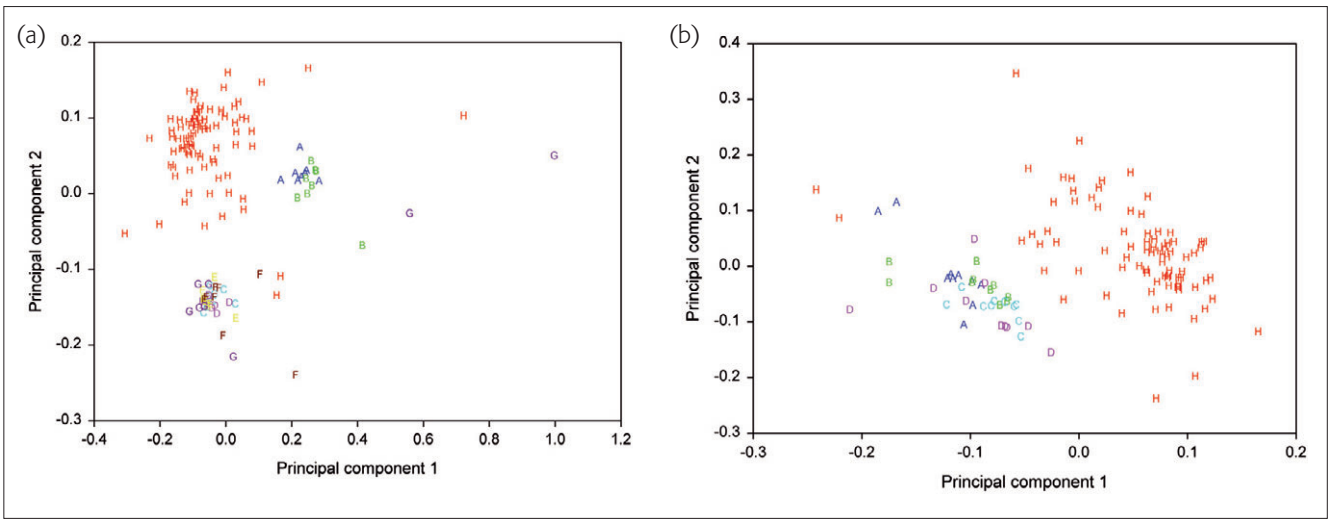

Figure 2. PCA scores plots of authentic and adulterated honeys. (a) Authentic (H) and beet invert syrup-adulterated honeys at 7 (A), 10 (B), 14 (C), 21 (D), 30 (E), 50 (F) and 70% w/w (G). (b) Authentic (H) and high fructose corn syrup-adulterated samples at 10 (A), 30 (B), 50 (C) and 70% w/w (D). (Reproduced by permission of NIR Publications).

1900 nm and around 2200 nm together with a slope variation in the region below approximately 1900 nm. The 2nd derivative spectra reveal large minima at 1442, 1930, 2278, 2324 and 2490 nm [Figure 1(b)]; smaller troughs are also evident at 1696 and 2112 nm and in the range between 2340 and 2450 nm. Absorbances at these wavelengths have been reported previously for solutions of glucose, fructose and sucrose.[1]

Each spectral set (honey plus BI-adulteratant and honey plus HFCS-adulterant) was subject to principal component analysis and the score plots for PC1 versus PC2 revealed a degree of sample clustering [Figures 2(a) and 2(b)]. It appears that, with the exception of three samples, pure honeys (H) cluster together and apart from the adulterated samples; some evidence of clustering on the basis of adulterant content is apparent in the case of beet invert sugar [Figure 2(a)], although not in the case of high fructose corn syrup [Figure 2(b)].

The actual problem to be addressed in this study is to confirm if a honey is authentic or not. SIMCA (soft independent modelling of class analogy) was utilised to develop a PCA-based model of authentic honeys (n=92), which was then applied to predict the identity of a different set comprising both authentic (n=46) and adulterated (n=96) honeys. All of the adulterated honeys were correctly identified as not authentic honey, only 90.9% of the authentic honeys were correctly classified. This result is, however, highly encouraging, particularly the finding that no false positive errors occurred. A loadings plot of the five components optimal for the model of authentic honey is shown in Figure 3. The major areas of importance are around 1440 and 1960 nm, the major absorbance bands of water which may be expected to undergo change as the concentration and chemical composition of sugar solutions change. Another area showing structured information lies between 2250 and 2350 nm approximately. This region has previously been reported to be involved in sugar absorbances.[1]

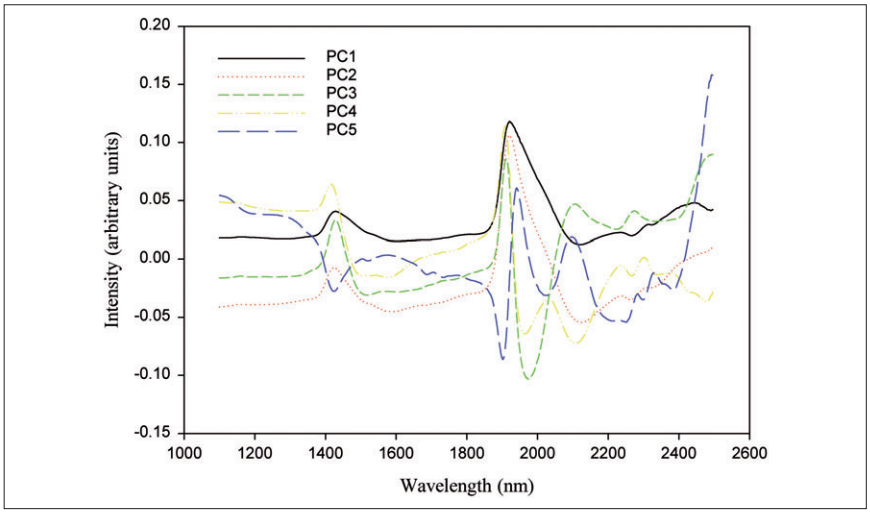

Figure 3. Plot of principal component loadings used in SIMCA model of authentic honey. (Reproduced by permission of NIR Publications.)

Samples identified as not being authentic may be subjected to more sophisticated analysis for confirmation and, while this takes time, the commercial protection obtained by the ability to identify all samples adulterated with either beet invert or high fructose corn syrup over a range of adulteration levels is significant and strongly suggests a useful role for NIR spectroscopy in this application. To extend the utility of this

work, further studies involving several other commercially-available sugar syrups are nearing completion.

Example 2: apple juice adulteration

Water and carbohydrates are the main components of apple juice; fructose, glucose and sucrose are the main carbohydrates with average concentrations of 5.6, 2.5 and 1.7% (w/w), respectively. Therefore, as is the case for honey, the majority of apple juice adulterations involve the substitution of juice solids with different types and combinations of sugar solutions or syrups. In a recent study,[2] the utility of NIR analysis for the detection and quantification of apple juice adulteration by added sugars was reported. Two different adulterants were used, i.e. (1) high fructose corn syrup (a commercial sweetener that approximates the carbohydrate composition of apple juice) and (2) an artificial mixture of sugars reflecting the average composition of apple juices. Predictive models were developed for each adulterant separately and for both combined.

Apple samples from 19 different varieties were collected from orchards throughout the main cultivation areas in Ireland. Two batches of samples were used in this study. A first group (n=68) was collected in December 2002 and January 2003; these apple samples were stored refrigerated (4°C) until February 2003 when the apple juice was extracted. A second set (n=82 samples) was obtained in October–November 2003 and juiced immediately. Two types of adulterant were used: a high fructose corn syrup (HFCS) with 45% fructose and 55% glucose, and a solution of sugars (SUGARS) made with 60% fructose, 25% glucose and 15% cane sucrose (the average content of these sugars in apple juice). Adulterant solutions were produced by dissolving sugars in distilled water up to 12°Brix, the average Brix content in apple juice samples. Adulterated juice samples were prepared with both types of adulterants, producing a total of 150 pure and 300 adulterated juices. Spectra were collected as described above using a 0.2mm sample thickness; raw and second derivative average spectra are shown in Figure 4.

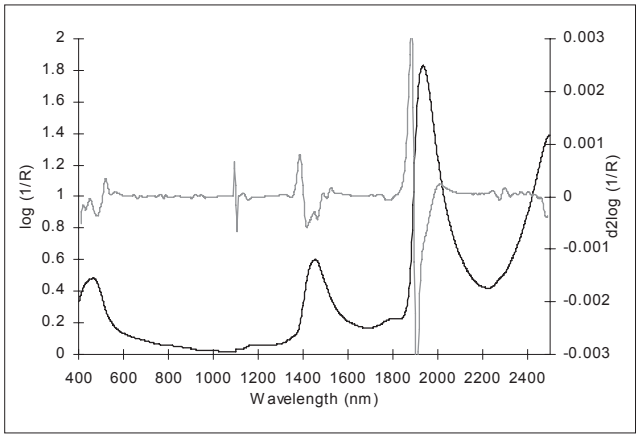

Figure 4. Average raw (black) and second derivative (grey) transflectance spectra of apple juices (the feature at 1100 nm in the second derivative spectrum arises from a detector change in the instrument). (Reproduced by permission of Society for Applied Spectroscopy from Reference 2.)

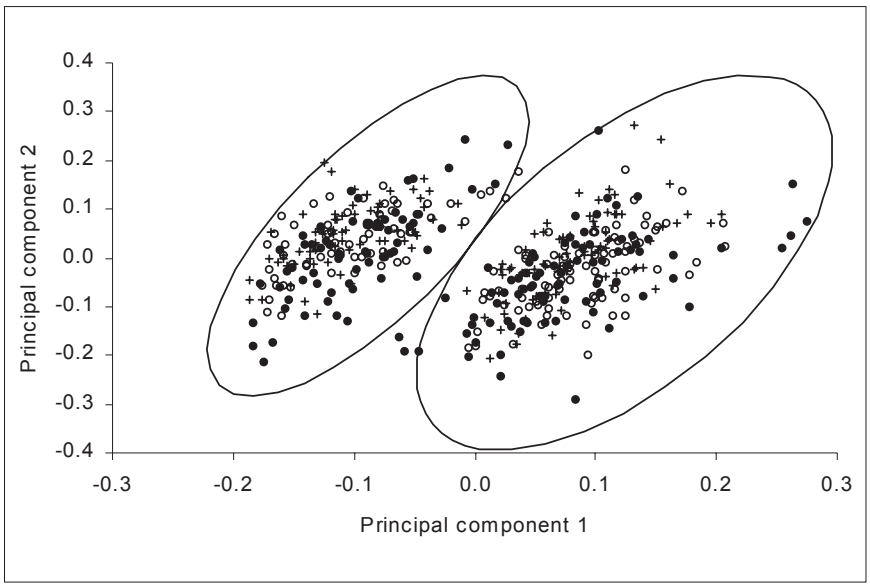

Figure 5. Principal component scores plot of 150 apple juice samples (•) and the same samples adulterated with HFCS (o) and SUGARS (+) solutions. (Reproduced by permission of Society for Applied Spectroscopy.)

Principal component analysis (PCA) was performed for a preliminary examination of the entire spectral dataset. The score plot for components 1 and 2, describing 42 and 31%, respectively, of the variance in the spectral collection, shows that, although no special grouping can be observed for pure and adulterated apple juices, two clusters can be clearly observed (Figure 5). This grouping is on the basis of the batch of apples used to produce the authentic juices and the two groups can be attributed to differences between both batches of samples. Factors such as cultivar, season, maturity or growing region can affect the characteristics of apple juices, especially in relation to sugar composition, but the different procedures used to obtain the apple juices may have significantly affected the composition of both groups of samples. In the first batch, the samples were stored refrigerated (4°C) for 1–2 months before the apple juices were extracted, whereas in the second batch the apple juices were obtained immediately after the collection of fruits. Significant differences in the sugar composition of juices made from fresh and stored apples have previously been reported: the sucrose content decreased while both the fructose and glucose concentrations increased on storage, indicating that sucrose was inverted.[3] Some sugar can be also lost through respiration in intact apples, thereby reducing the total carbohydrate content.[3] Rather than a weakness, this variation in storage time is a variable that occurs in practice and would be required to be included in reference sample sets used in authenticity tests or quantitative model development.

Discriminant Partial Least Squares (PLS) regression was studied as a method for discriminating between authentic and adulterant apple juices. This tool was applied separately for each adulterant type and for combined adulterants using the whole wavelength range (400–2500 nm) after multiplicative scatter correction of data. A summary of the results obtained is shown in Table 1. The most practically-useful model is that for detecting either type of adulteration, i.e. combined; this reveals a correct classification rate of 96% for adulterated juices but a lower value (86%) for authentic juices. Higher correct classification rates for authentic juice were reported for individual adulterants. Nonetheless, this represents a useful outcome given that the greatest danger for a food processor or retailer is the inadvertent use of an adulterated juice; samples identified as adulterated by this model may be referred for further analysis to confirm their authenticity.

Table 1. Apple juice classification by PLS1 models developed separately for each level and adulterant type and for both adulterants in combination.

		Unadulterated apple juice		Adulterated apple juice	
Adulterant	# of loadings	# of samples	% correctly classified	# of samples	% correctly classified
HFSC	11	150	98	150	91
SUGARS	11	150	91	150	93
Combination	13	150	86	300	96

Summary

These results show that NIR spectroscopy has the potential to act as a screening method for confirming the authenticity of honey and apple juice samples, although elucidation of the molecular basis for any classification models remains difficult. Previous work has reported this potential for foods such as meat and olive oil. Further studies with significantly enlarged sample sets are required to demonstrate this capability in the market place and several such investigations are currently underway in the EU-funded integrated project "TRACE" (www.trace.eu.org) so watch this space for future updates.

References

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