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Application of Fourier Transform Midinfrared Spectroscopy to the Discrimination between Irish Artisanal Honey and Such Honey Adulterated with Various Sugar Syrups

J. Daniel Kelly,† Cristina Petisco,‡ and Gerard Downey*,†

Teagasc, Ashtown Food Research Centre, Ashtown, Dublin 15, Ireland, and Instituto de Recursos Naturales y Agrobiología, Consejo Superior de Investigaciones Científicas, Apdo. 257, 37071 Salamanca, Spain

A collection of authentic artisanal Irish honeys ($n = 580$) and certain of these honeys adulterated by fully inverted beet syrup ($n = 280$), high-fructose corn syrup ($n = 160$), partial invert cane syrup ($n = 120$), dextrose syrup ($n = 160$), and beet sucrose ($n = 120$) was assembled. All samples were adjusted to 70 °Bx and scanned in the midinfrared region (800−4000 cm^{-1}) by attenuated total reflectance sample accessory. By use of soft independent modeling of class analogy (SIMCA) and partial least-squares (PLS) classification, authentic honey and honey adulterated by beet sucrose, dextrose syrups, and partial invert corn syrup could be identified with correct classification rates of 96.2%, 97.5%, 95.8%, and 91.7%, respectively. This combination of spectroscopic technique and chemometric methods was not able to unambiguously detect adulteration by high-fructose corn syrup or fully inverted beet syrup.

KEYWORDS: Adulteration; honey; FTIR; authenticity; sugar syrups; chemometrics

INTRODUCTION

Honey is defined in European legislation as "the natural sweet substance produced by honeybees from the nectar of plants or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in the honeycomb to ripen and mature" (*1*). It is similarly described in the Codex Alimentarius of the Food and Agriculture Organization of the United Nations (*2*), while countries in which Codex has not been adopted have definitions that are almost identical. As a result of its natural provenance and the range of health-giving and antiseptic properties ascribed to it, it is highly desired by consumers in many countries (*3*). Artisanal honey produced in the traditional manner by individuals with small numbers of hives is particularly highly prized, especially when it is unifloral in nature.

On account of the limited production of such honeys, they command a premium price and thereby become a potential target for food adulteration. This may be achieved, for example, by extension of honey through the addition of sweet substances such as sugars or industrial syrups at some stage during production or processing. In an effort to identify one or more markers exclusive to such adulterants and thereby detect adulteration, a wide range of analytical techniques has been deployed, for example, nuclear magnetic resonance (NMR) spectroscopy (*4*), high-performance liquid chromatography (HPLC) (*5*, *6*), gas chromatography (GC) (*7*), and carbon isotope ratio analysis (*8*, *9*). These methods are, however, time-consuming, destructive, and generate significant costs associated with reagent purchase and byproduct disposal. There is therefore a need for a rapid, economic, and nondestructive procedure for screening of honeys to facilitate the detection of adulterated product by processors, retailers, and regulatory agencies with a high level of confidence. Vibrational spectroscopic methods (near- and midinfrared), in combination with multivariate data analysis, possess the speed, simplicity, and low cost per analysis required for such screening techniques; they have previously been applied to a range of food authenticity problems (*10*−*16*). With respect to honey, they have been used to determine chemical composition (*17*−*21*), and their application to the detection of honey adulteration by various individual sugar syrups has also been reported in a series of individual publications (*21*−*28*). Success rates quoted in these reports have varied depending on adulterant.

This paper reports the use of midinfrared spectroscopy for the classification of Irish artisanal honeys as either authentic or adulterated with one of five potential adulterant sugar syrups: fully inverted beet syrup, high-fructose corn syrup, partial invert cane syrup, dextrose syrup, and beet sucrose solutions.

MATERIALS AND METHODS

Samples. Honey samples ($n = 580$) were obtained directly from beekeepers throughout the island of Ireland during the years 2000−2003; they were stored unrefrigerated from time of production until

* To whom correspondence should be addressed: tel +353-1-8059500; fax +353-1-8059550; e-mail gerard.downey@teagasc.ie.
† Teagasc, Ashtown Food Research Centre.
‡ Instituto de Recursos Naturales y Agrobiología, CSIC.

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Table 1. Breakdown of Sample Numbers on the Basis of Year of Honey Production and Adulterant Type

	honey production year				
sample type	2000	2001	2002	2003	total
honey	108	241	130	101	580
CS-adulterated	62	48	29	21	160
HFCS-adulterated	19	49	59	33	160
IB-adulterated	48	124	67	41	280
PICS-adulterated	12	4	57	47	120
BS-adulterated	9	8	59	44	120

scanning and were not filtered after receipt in the laboratory. The lack of refrigeration carries the risk that the honey samples will have changed between removal from the hive and spectral analysis; however, the inclusion of such changes reflects the reality that any successful model should be able to accommodate variations in honey age and should improve the robustness of predictive models developed. Immediately prior to spectral collection, honeys were incubated at 40 °C overnight to dissolve any crystalline material, manually stirred to ensure homogeneity, and adjusted to a standard solids content (70 °Bx) with distilled water (also at 40 °C) to avoid spectral complications from naturally occurring variations in sugar concentration. Adulterant solutions were adjusted to 70 °Bx by diluting commercially sourced, fully inverted beet syrup (IB; 50:50 fructose/glucose; Siúcra Eireann Teo, Carlow, Ireland), high-fructose corn syrup (HFCS; 45% fructose and 55% glucose; Unilever Ireland Ltd.), partial invert cane syrup (PICS; 32:32:36 fructose/glucose/sucrose; Tate & Lyle Golden Syrup), and dextrose syrup (CS; Leaf Gum Ltd, Ireland) with distilled water. Beet sucrose (BS) solutions were prepared by dissolving beet sugar (Siúcra Eireann Teo, Carlow, Ireland) in distilled water at 70 °Bx. Pure honeys were adulterated in batches of 40 with an adulterant solution at the following levels (% w/w); HFCS, 10, 30, 50, and 70; IB, 7, 10, 14, 21, 30, 50, and 70; PICS, 10, 20, and 30; BS, 10, 20, and 30; CS, 7, 14, 21, and 30. This produced a total of 840 adulterated honey samples; each of these was produced with a different authentic honey sample. **Table 1** gives a breakdown of samples according to the year of honey production and adulterant type. Adjustment of adulterant solutions to 70 °Bx prior to honey adulteration meant that any segregation detected in this work would not be caused by differences in gross solids content.

Instrumentation. Solids content in honeys and adulterated solutions was measured by refractometry in an Abbé model 2WA benchtop refractometer. Midinfrared spectra were collected at room temperature on a Bio-Rad Excalibur series FTS 3000 spectrometer (Analytica Ltd., Dublin, Ireland); instrument control and spectral collection were performed with WIN-IR Pro (v 3.0) software supplied by the equipment manufacturer. Spectra were recorded on an in-compartment benchmark attenuated total reflectance (ATR) trough top plate by use of a 45° Ge crystal with 11 internal reflections. Sixty-four scans were coadded at a nominal resolution of 4 cm^{-1}. Single-beam spectra of the samples were collected and ratioed against a background of air. Spectra were truncated to the useful range of the Ge ATR crystal (800−4000 cm^{-1}) and then converted to a wavelength scale (2500−12 500 nm) with the supplied Win-IR Pro software. Between samples, the crystal was cleaned with tepid water and dried with lens cleaning tissue; the spectral baseline recorded by the spectrometer was examined visually to ensure that no residue from the previous sample was retained on the crystal. All spectra were recorded in duplicate, from separate subsamples, at a room temperature between 20 and 25 °C. Averages of these duplicates were used in data analysis.

Data Analysis. Spectra were exported from WIN-IR Pro as GRAMS files (ThermoGalactic, Salem, NH) and imported directly into The Unscrambler (v8.0; CAMO ASA, Oslo, Norway) or Pirouette Lite Classify (v3.10; Infometrix Inc., Bothell, WA). Models were developed for the spectral region between 6800 and 11 500 nm (870−1471 cm^{-1}), which is dominated by information on the sugar composition (*28*, *29*). Principal component analysis (PCA) was performed in The Unscrambler to detect unusual spectra and any clustering in the data set that might be visible. Calibrations generated for classifications were developed and evaluated on separate calibration and prediction sample sets. Samples were assigned to these sets based on their position in the spectral file. All odd-numbered samples were assigned to the calibration sample set and all even-numbered samples to the prediction sample set. Partial least-squares (PLS1) regression (The Unscrambler) onto a dummy variable was used for discrimination between authentic and adulterated samples. The dummy variable was assigned a value of −1 for an authentic honey sample and +1 for all other samples. A cutoff point of 0 was chosen for the discrimination predictions. Classification was also attempted by the *k*-nearest neighbor (*k*-NN) and soft independent modeling of class analogy (SIMCA) methods with Pirouette software. Class cutoff limits in SIMCA were set at the 5% level. Calibration and prediction sample sets were the same as those used in PLS analyses.

For quantitative analysis by PLS1, the *y*-variable was assigned the value of the adulterant content. Spectral data pretreatments examined were first- and second-derivative spectral data using the Savitsky−Golay method and a segment size of 5 data points. Full cross-validation was used in model development, with the optimal models being applied to the relevant prediction sample set. Only optimal models are discussed in this paper.

RESULTS AND DISCUSSION.

The average raw and second-derivative midinfrared ATR spectra of 50 randomly selected authentic honey samples are shown in **Figure 1**. The midinfrared spectrum of honey is dominated by sugar absorptions; the most significant features of the raw spectra are peaks at 8713, 9460, and 9680 nm approximately and shoulders centered around 9080, 9300, and 10 180 nm. These broad features are narrowed in the second-derivative spectra, which reveal considerable structure across the entire spectral range plotted; particularly strong absorptions are found in the range 8690−10 360 nm. Bands appearing between 6800 and 8700 nm are due to bending modes of C−C−H, C−O−H, and O−C−H groups (*29*). The more intense peaks in the region around 8700−11 000 nm arise mainly from C−O and C−C stretching modes (*29*), with a peak around 9400−9800 nm due to O−H vibrations (*30*). At longer wavelengths, bands due to C−H and O−H bending vibrations may also be useful for discrimination and quantification purposes. Fructose and glucose are the major components of honey and exhibit maximum absorbances at ∼9490 nm (fructose) and ∼9820 nm (glucose). As a result of the differences observed between the spectra of the major components of honey (fructose, glucose, and sucrose), midinfrared spectroscopy has been used for the accurate determination of the sugar composition of mixtures and syrups (*31*−*33*).

Raw and second-derivative spectra of an authentic honey and honey samples adulterated with each of the sugar syrups at the highest adulteration level are shown in **Figure 2**. Some differences between these spectra may be seen, particularly around each of the peaks or shoulders mentioned above; BS-adulterated honey seems to show the most significant differences. However, as the spectral variations in honey samples can also be quite large (**Figures 1**), identification of authentic samples by visual analysis of test sample spectra is impossible. Chemometric data analysis techniques are therefore necessary to discriminate between authentic and adulterated samples.

Preliminary Data Analysis. The entire set of spectra was input to a principal component analysis to check for unusual or outlying samples and to determine if any clustering of samples on the basis of adulteration or even adulterant type was apparent. The best clustering observed was obtained with second-derivative spectra, and some results of this PCA are shown in the score plots shown in **Figures 3** and **4**. **Figure 3** reveals the

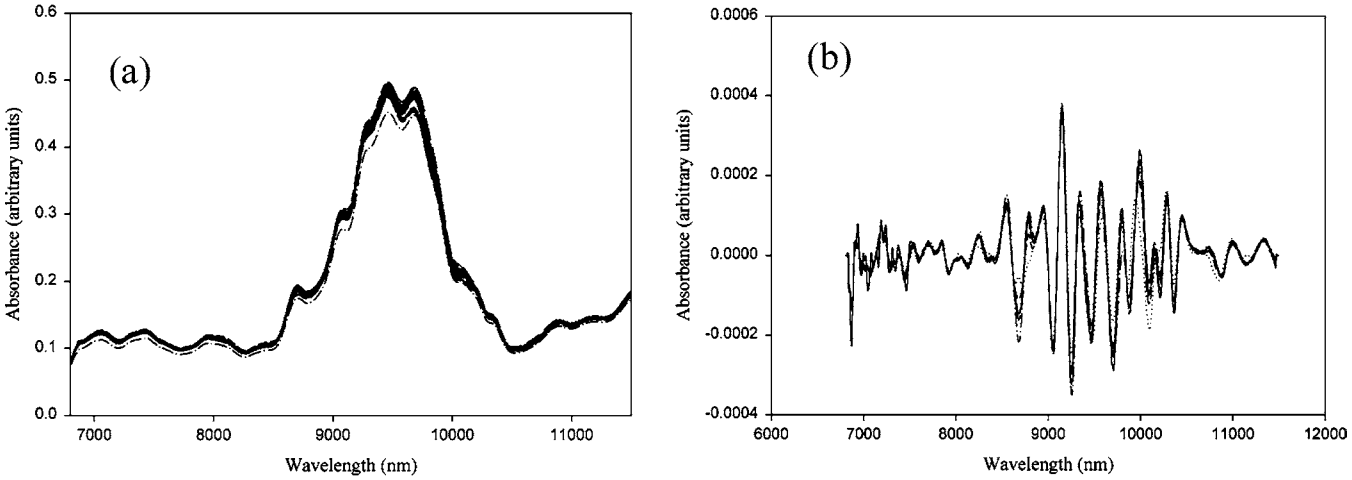

Figure 1. Midinfrared ATR spectra of a random selection of authentic Irish honeys: (**a**) raw spectra; (**b**) second-derivative spectra.

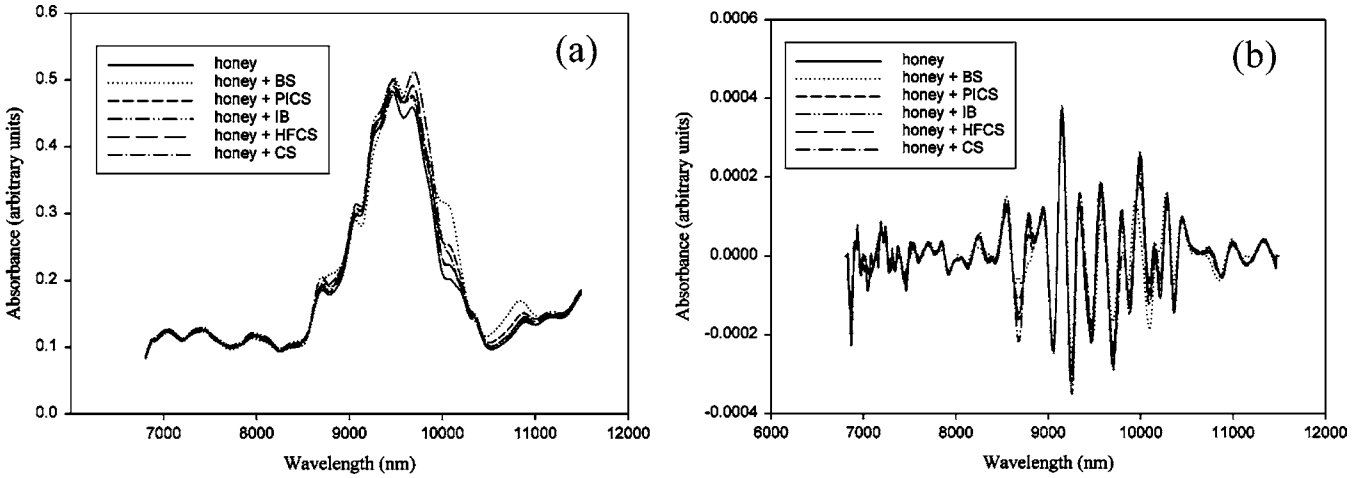

Figure 2. Midinfrared ATR spectra of randomly selected authentic and adulterated Irish honey: (**a**) raw spectra; (**b**) second-derivative spectra.

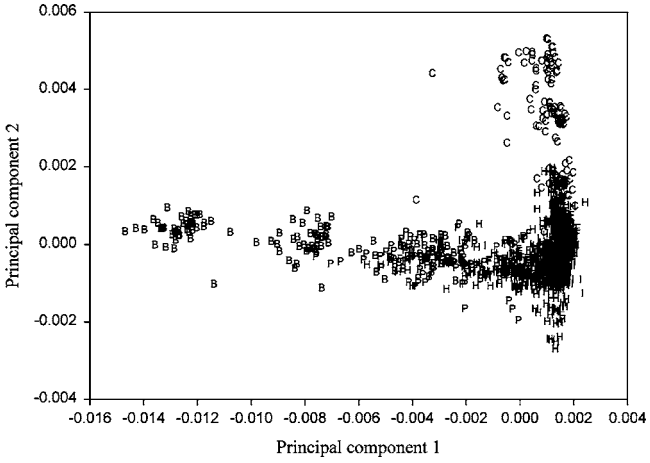

Figure 3. Scores plot of all samples on principal components 1 and 2; calculated from second-derivative mid-IR spectra (B = beet sucrose adulterant; C = dextrose syrup adulterant; H = authentic honey; P = partial invert cane syrup adulterant; I = fully inverted beet syrup adulterant).

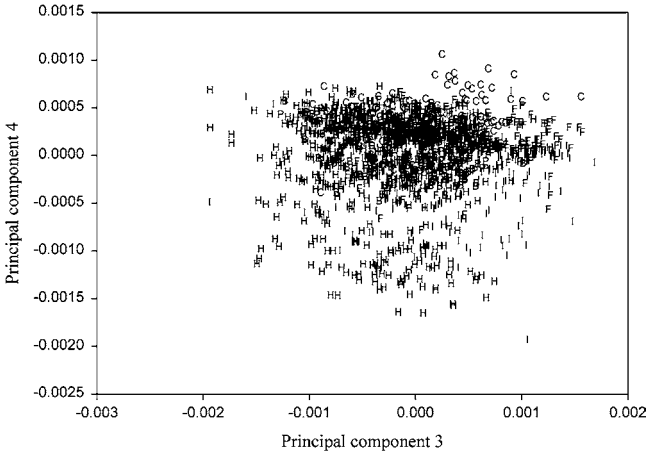

Figure 4. Scores plot of all samples on principal components 3 and 4; calculated from second-derivative mid-IR spectra (B = beet sucrose adulterant; C = dextrose syrup adulterant; H = authentic honey; P = partial invert cane syrup adulterant; I = fully inverted beet syrup adulterant).

main sources of variance in the spectral collection to arise from samples adulterated with beet sucrose and dextrose syrup; the former defines eigenvector 1 while the latter is mainly responsible for eigenvector 2. Clustering of the beet sucrose-adulterated samples corresponds to the different inclusion levels of this syrup; similar behavior is noticeable with the dextrose syrup-adulterated honeys. There is a suggestion that honeys adulterated with partial invert cane syrup may also be clustering slightly apart from the main sample group. Some degree of separation of the authentic honeys from the remainder of the samples may be seen in **Figure 4** on the basis of sample scores on eigenvector 4. Features of principal component 1 (**Figure 5**) that contribute to the separation of the beet sucrose separation may be noted at around 7524, 7668, 7786, 7825, and 7922 nm; in the case of

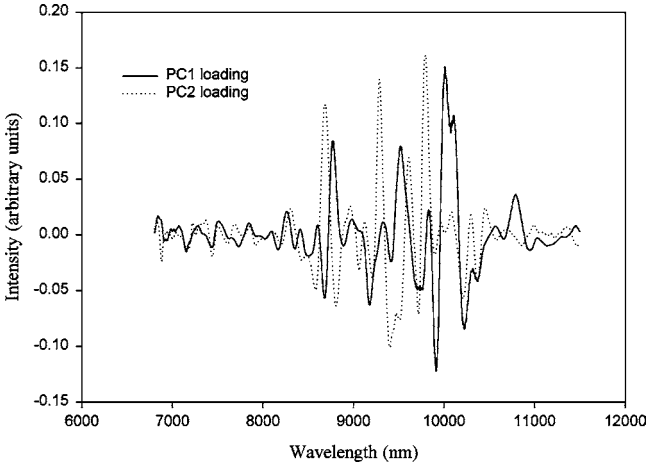

Figure 5. Eigenvectors of principal components 1 and 2 calculated from second-derivative midinfrared spectra of all honey samples (authentic plus adulterated).

Table 2. Classification Prediction Results from SIMCA Modeling of Authentic Honeys[a]

sample type	no. of samples	no. correctly identified	no. incorrectly identified	% correctly identified	% incorrectly identified
honey	290	279	11	96.2	3.8
BS-adulterated	120	117	3	97.5	2.5
PICS-adulterated	120	62	58	51.2	48.3
CS-adulterated	120	115	5	95.8	4.2
HFCS-adulterated	160	2	158	1.3	98.8
IB-adulterated	280	19	241	6.8	93.2

[a] Second-derivative spectra.

dextrose syrup, features at 7487, 7717, 7910, 7940 (shoulder), 8151, and 8411 nm are important.

Classification. The initial strategy explored was to develop a SIMCA model of authentic honeys and evaluate the performance of this model on different authentic honeys plus all of the adulterated samples. A SIMCA model (with six PCs) was developed on 290 authentic honeys with the test sample file containing 290 authentic and 800 adulterated samples; classification results for the test samples are shown in **Table 2**. These results show that 96.2% of authentic honey samples were correctly identified; additionally, 97.5% of BS-adulterated and 95.8% of CS-adulterated honeys were correctly identified as not being authentic honey. This shows that the model may be used to confirm authenticity in Irish artisanal honeys and such honeys adulterated with beet sucrose or dextrose syrup at levels used in this study, that is, down to minimum levels of 10% and 7% (w/w), respectively. On the other hand, approximately half of the PICS-adulterated samples and almost all of the HFCS-adulterated (98.8%) and IB-adulterated (93.2%) samples were wrongly classified as honey; this result stems from the similarity in monosaccharide composition of honey and these syrups. This particular classification therefore only produces highly accurate results for the BS- and CS-adulterated samples.

The next stage was to develop SIMCA models for BS- and CS-adulterated honeys to determine if these could be separately identified. For this purpose, a SIMCA model was developed for each with 50% of the relevant samples; these models were then used to predict the identity of all of the other similarly adulterated samples. Results obtained are shown in **Table 3** and show that the type of adulterated honey can be identified with a very high level of certainty. In the case of the CS-adulterated honey model, 100% of the BS-adulterated solutions were correctly identified, as were 96.7% of the CS-adulterated samples. When the BS-adulterated model was applied to samples classified by the honey SIMCA model as nonauthentic honeys, 96.7% of BS-adulterated samples were correctly classified, as were 99.9% of the CS-adulterated material.

Table 3. Classification Prediction Results from SIMCA Modeling of CS- and BS-Adulterated Honeys[a]

	CS-adulterated model			BS-adulterated model		
sample type	no. of samples	no. correctly identified	no. incorrectly identified	no. of samples	no. correctly identified	no. incorrectly identified
BS-adulterated	120	120	0	60	57	3
CS-adulterated	60	58	2	120	119	1

[a] Second-derivative spectra.

Given that the adulteration of honey by both these adulterants can be detected with a high degree of confidence, the possibility of quantifying the inclusion level of the adulterants was addressed. For each adulterant type, this was achieved by use of PLS1 regression of second-derivative spectral data; given the relatively small number of samples involved, calibrations were developed and evaluated by full (i.e., leave-one-out) cross-validation. In the case of BS adulteration, the inclusion level of beet sucrose could be detected with a root mean standard error of cross-validation (RMSECV) equal to 2.1; the associated correlation coefficient and slope of the fitted regression line were 0.97 and 0.94, respectively. For dextrose syrup quantification, the RMSECV, correlation coefficient and fitted regression line slope were equal to 1.1, 0.98, and 0.96, respectively. These accuracy levels are sufficiently low as to be industrially useful.

The remaining problem with this data set was to discriminate between authentic honey and honey adulterated with either IB, HFCS, or PICS syrups. One way of approaching this problem is to set up a series of binary decisions. Therefore, a set of discriminant PLS models was developed for authentic honey and each of the adulterated honey types. As an example, a PLS1 model involving nine loadings was developed to distinguish between authentic honey and honey adulterated with PICS syrup. To do this, all of the honeys of each type were subjected to PLS1 against a dummy variable with full cross-validation. The outcome of this procedure was that 99.1% and 91.7% of authentic and PICS-adulterated honeys were correctly classified. When the model was applied to honey adulterated with HFCS or IB, 92.5% and 94.3% of these honey types respectively were identified as not PICS-adulterated honeys, that is, they were incorrectly classified as authentic honeys. Nonetheless, this step allows confirmation of the identity of PICS-adulterated honey with a very high (91.7%) classification accuracy and therefore confidence level.

When this approach was extended to try to identify honeys adulterated with HFCS or IB, the results were less accurate. In the case of the authentic versus IB-adulterated honey model, which involved nine loadings, although 98.3% of authentic samples were correctly classified, only 76.4% of the IB-adulterated honeys were identified as such. However, 90.6% of HFCS-adulterated samples were identified as other than IB-adulterated. Similarly, when a HFCS-adulterated versus authentic honey model (seven loadings) was developed, only 68.8% of HFCS honeys were correctly classified and 66.8% of IB-adulterated samples were identified as non-HFCS-adulterated material. An alternative approach investigated was to develop a classification model for these three sample types using

Table 4. Classification Results for *k*-Nearest Neighbor ($k = 6$) Modeling of Authentic Honeys and Honeys Adulterated with HFSC and IB[a]

	calibration sample set		prediction sample set	
honey type	no. of samples	% correct classification	no. of samples	% correct classification
authentic	194	91.2	386	87.8
HFCS-adulterated	80	71.3	80	75.0
IB-adulterated	140	70.0	140	71.4

[a] Second-derivative spectra.

k-nearest neighbor analysis. To minimize difficulties arising from the sensitivity of this particular technique to inequalities in sample set size, a classification model was developed on a calibration sample set comprising approximately $^1/_3$ of authentic honeys ($n = 194$) and half each of the HFCS- and IB-adulterated samples, $n = 80$ and 140, respectively. This model was then evaluated on the remainder of the samples and the overall results are shown in **Table 4**. The percentage correct classification in both the calibration and prediction sample sets agree well, indicating the validity of the *k*-NN model. However, while the correct classification rate for authentic honeys is quite high at 87.8% in the prediction set, that for both adulterated sample types is lower at 75% (HFCS) and 71.4% (IB), respectively. These results are unlikely to be commercially useful and indicate the difficulty in discriminating between these sample types by midinfrared ATR spectra. Greater success has been reported in this discrimination with near-infrared spectroscopy (*28*); 100% of adulterated and 90.9% of unadulterated honeys were correctly classified by a SIMCA (soft independent modeling of class analogy) approach, although the sample numbers involved in the NIR study were smaller (79 unadulterated and 96 adulterated).

Conclusions. By use of ATR mid-infrared Fourier transform spectra, it has been possible to discriminate between authentic Irish artisanal honeys and such honeys adulterated by dextrose, partial invert cane, and beet sucrose syrups by a decision tree approach. The levels of accuracy reported suggest that these models may have commercial value. Efforts to discriminate between authentic samples and honeys adulterated with either high-fructose corn syrup or fully inverted beet syrup were not so successful, and it is unlikely that midinfrared spectroscopy will be the method of choice for their identification.

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