Use of Infrared Spectroscopy and Chemometrics for the Authentication of Fruit Purees

Marianne Defernez,* E. Katherine Kemsley, and Reginald H. Wilson

Institute of Food Research, Norwich Laboratory, Norwich Research Park, Colney, Norwich NR4 7UA, United Kingdom

Fourier transform infrared spectroscopy in combination with discriminant analysis (DA) was used to classify fruit purees into three predefined groups, namely strawberry, raspberry, and apple. Using optimized parameters, 149 spectra subjected to this analysis were classified with 100% success. A separate analysis of each set of fruit was able to distinguish with 98.3% success for strawberry and 75% for raspberry, whether the fruits were fresh or freeze–thawed. Classification according to two levels of ripeness also gave good results (92.5% correctly classified) for raspberry but not for strawberry. With apple purees, DA was able to identify if sulfur dioxide had been added or not (90% correctly classified) and if the variety was Bramley or not (86% correctly classified).

Keywords: *Infrared; spectroscopy; authenticity; fruit*

1. INTRODUCTION

The authentication of food is an important issue for both the consumer and the food industry, at all levels of the food chain, from raw material to finished products. From a legislative point of view, minimum standards of quality have been established along with labeling legislation, which requires the composition of every product to be specified. From an economic point of view, it is essential that the raw materials are authentic to avoid unfair competition which would disrupt the market. Fruit purees are used in the production of jams and are the only form used for fragile fruits like raspberry. Purees are cheaper than whole fruits, but their authenticity is more difficult to establish. For instance, a possible method of adulteration is their partial substitution with cheaper constituents, such as other fruits, vegetable matter, sugar, or water.

The detection of such adulteration often requires the use of lengthy wet chemical procedures. Infrared spectroscopy has recently been shown to be sensitive to the species and amount of fruit used in jams (Wilson et al., 1993). Therefore, this study was carried out to investigate the potential of this technique for the authentication of fruit purees.

The identification of different species, cultivars, or processing conditions for fruit juices and concentrates has been addressed using a variety of methods. These methods rely on the identification of a specific compound that should not be present or on the determination of the "normal concentration range" of one or several compounds, as explained by Konja and Lovric (1993). The abnormal presence of a component in a puree as a result of dilution with another fruit can sometimes be detected by microscopic observation if the cells of fruits present have characteristic shapes or appearance. Genetic methods have also been used to identify apple cultivars (Koller et al., 1993). However, most of the research is based on the separation and quantification of a number of constituents. For example, the analysis of red raspberry juice by HPLC (Rommel et al., 1992; Rommel and Wrolstad, 1993a,b) led to the definition of the normal concentration ranges of phenolics, flavonols, and ellagic acid. Various chromatographic methods were used for the quantification of anthocyanins in fruit juices and purees, as shown by Lee and Hong (1992). The comparison of the amounts of several compounds to their normal ranges can be used as a means of detecting adulteration. Much research has also been conducted on the effect of storage and processing. For instance, the influence of different storage temperatures of red raspberry juice concentrate on its anthocyanin level was investigated (Withy et al., 1993), as was the influence of the atmosphere of storage, of clarification, and of the addition of SO_2 or EDTA (Bakker et al., 1992; Bakker and Bridle, 1992). Gas chromatography was also used to quantify the main sugars and acids in fruit and vegetables, and the effects of ripening, clarification, and concentration were studied (Molnar-Perl and Morvai, 1992).

The aim of the work presented in this paper was to develop a method to differentiate purees of different fruits, as a first step in creating a rapid method for detecting adulterated samples. Difficulties in solving discrimination problems arise from the fact that the samples are often composed of the same basic constituents. Therefore, the consideration of only one analytical parameter is not sufficient, and the use of a combination of several such parameters is often necessary. Fourier transform infrared spectroscopy can provide this information, in the form of a spectrum, in a very short time, which is a major advantage over the separation methods traditionally used. Horizontal attenuated total reflectance (HATR) was chosen as the sampling technique for its ease of use (Belton and Wilson, 1990).

Chemometric methods are increasingly used for solving problems in which several groups, or species, are to be differentiated and are particularly suited for the analysis of large data sets. They have been used for differentiating species of wood (Nault and Manville, 1992), and for analyzing the basis of the botanical classification of *Acacia* (Vulgares and Gummiferae) and related natural gums (*Albizia, Combretum*) (Jurasek et al., 1993). In food systems, they have been applied to the differentiation of honeys of two geographical origins (Pena Crecente and Herrero Latorre, 1993), as well as brandies of different nationalities (Schreier and Reiner, 1979), milk from different animal species (Smeyer-

* E-mail Marianne.Defernez@BBSRC.AC.UK.

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Verbeke et al., 1977), and peppermint oils of different origins (Chialva et al., 1993). As far as fruits are concerned, the origin of orange juice and frozen concentrated orange juice (Florida or Brazil) was investigated (Nikdel et al., 1988; Bayer et al., 1980).

In the study presented here, infrared spectra of fruit purees were classified into three groups (strawberry, raspberry, and apple). The procedure consisted of two steps: First, a principal component analysis (PCA) (Massart and Kaufman, 1983) was carried out. PCA provides a method of highlighting differences in the superficially similar spectral data (Lai et al., 1994) by reducing the dimensionality of the set (Howells et al., 1992; Hobert and Meyer, 1992) and, in addition, overcomes problems caused by correlations between variables. Second, the PC scores produced were used to perform a discriminant analysis (DA) based on the distances of the sample from the group "mean" of each predefined group, as described by Howells et al. (1992). Using the same method, the individual fruits were also studied in more detail to measure the sensitivity to a number of parameters such as whether purees were from fresh or freeze–thawed fruit.

2. MATERIALS AND METHODS

2.1. Samples. Most strawberry and raspberry purees were obtained from fruits collected in local self-pick fields. The fruits were collected from two different sites, weekly over a period of 5 weeks. Five different varieties of strawberry (Bogota, Cambridge Favourite, Elsanta, Hapil, and Kouril) and five of raspberry (Augusta, Glen Moy, Malling Jewel, and two unknown varieties) were obtained. Fruits were collected at two levels of ripeness (ripe and underripe), as judged by the color. After collection, some of the fruits were processed into purees and analyzed immediately. The remaining fruits were frozen at −30 °C and analyzed after warming to room temperature. Additionally, a number of strawberry and raspberry samples were obtained from industrial sources. These samples were delivered frozen, either as whole fruits or as purees, with some purees being aseptically packed. Whole strawberries and raspberries were transformed into a puree, after defrosting, by pushing through a metal sieve.

Most apple purees were obtained from fruits bought in local supermarkets, and a large range of varieties was used (Braeburn, Bramley, Cox, Early Red, Fuji, Golden Delicious, Granny Smith, Grenadier, Jonagored, Red Delicious, Royal Gala, Sturmer Pippin, and Top Red). They were stored at 1 °C and allowed to warm to room temperature before processing. Some apple samples were also obtained from industrial sources, either as fresh fruits or as purees containing sulfur dioxide. All whole apples were processed into a puree in a coffee bean grinder (Krups 50); the cores were removed, and two purees were prepared for each apple, one with and one without the peel. The number of samples and subsequent spectra recorded of each fruit type are summarized in Table 1.

2.2. Instrumentation. All spectra were collected on a Spectra-Tech (Applied Systems Inc.) MONITIR FTIR spectrometer system, fitted with an air-cooled infrared source (tungsten carbide), a sealed and desiccated interferometer, and a deuterated triglycine (DTGS) detector. One of two dedicated sampling stations was equipped with an overhead ATR accessory, which comprised transfer optics with a desiccated chamber sealed from the atmosphere by two potassium bromide windows. Through these windows the infrared radiation was directed into the detachable ATR element. The element used was a 10-reflection zinc selenide crystal mounted into a plate with a shallow trough for sample containment. The crystal geometry was a 45° parallelogram with mirrored angle faces.

2.3. Spectral Acquisition. The purees were spread directly onto the ATR element. Spectra were obtained of all purees. Frozen samples were thawed to room temperature before acquisition. The spectra were recorded from 800 to 4000 cm^{-1} at a resolution of 8 cm^{-1}. For each spectrum, 256 interferograms were co-added and a triangular apodization was employed before Fourier transformation. A single-beam spectrum of water was also collected under identical conditions for transforming the puree spectra into absorbance units.

Table 1. Numbers and Types of Samples and Spectra

	samples			spectra	
fruit	source	maturity	*N*	condition	*N*
strawberry	picked	ripe	15	fresh	15
				thawed	15
		underripe	15	fresh	15
				thawed	15
	industrial source		7	thawed	7
raspberry	picked	ripe	10	fresh	10
				thawed	10
		underripe	10	fresh	10
				thawed	10
	industrial source		3	thawed	3
apple	bought		17	pulp	17
				pulp and peel	16
	industrial source		5		6

Table 2. Composition of the Subsets Used in the Cross-Validation Procedure

	strawberry					raspberry					apple	
	fresh		freeze-thawed			fresh		freeze-thawed				
subset	*a*	*b*	*a*	*b*	*c*	*a*	*b*	*a*	*b*	*c*	pulp	pulp and peel
1	2	2	3	2	1	3	1	1	2	0	3	3
2	2	3	2	2	0	1	2	1	1	1	3	3
3	2	2	2	2	1	2	1	1	2	0	3	3
4	2	2	3	2	1	1	2	2	1	0	3	3
5	2	2	2	2	1	1	1	1	2	1	2	3
6	2	2	2	2	1	0	2	2	1	1	3	2
7	2	2	1	3	1	2	1	2	1	0	2	3

[a] Hand-picked, ripe. [b] Hand-picked, underripe. [c] Obtained from industrial sources, ripeness uncertain.

2.4. Chemometrics. Data analysis was carried out using both SPIDA (Statistical Package for Interactive Data Analysis) software (Statistical Computing Laboratory, NSW, Australia) and Win-Discrim (K. Kemsley, Norwich), a specialized package for discriminant analysis.

For each spectrum 311 data points were considered, corresponding to the 800–2000 cm^{-1} region, which was the information-rich region. The analyses were carried out with both single-beam and absorbance spectra, and they were preceded or not by an area normalization of the spectra.

The first part of the analysis investigated the discrimination between purees produced from different fruit species: 149 spectra were examined, comprising 67 strawberry purees, 43 raspberry purees, and 39 apple purees. Two parameters were used to assess the robustness of the classification procedure, as described by Massart et al. (1988), the recognition ability, and the prediction ability.

The estimation of the recognition ability involved performing a PCA on the 149 spectra (i.e. on a 149 × 311 data matrix) and using the scores in a DA to classify the samples into three categories (strawberry, raspberry, and apple). The estimation of the prediction ability involved the use of training and test sets, in a procedure called "cross-validation" as explained by Martens and Naes (1989). This consisted of dividing the total 149 spectra set into 7 subsets, each representative of the total set of spectra, as shown in Table 2. The validation process involved excluding one subset of data and creating a model with the six other subsets and then validating the model with the excluded subset. The procedure was repeated seven times, excluding each subset in turn.

The second part of the study was the examination of the sets of individual fruit purees by a similar method to analyze the efficiency of the classification according to various characteristics of the fruit such as whether it was fresh or had been

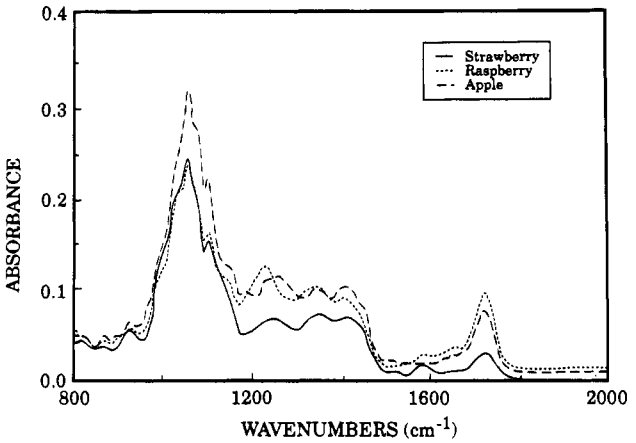

Figure 1. HATR spectra of various fruit purees.

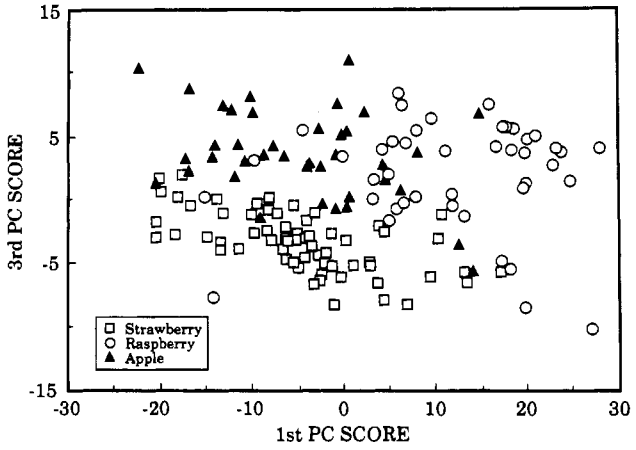

Figure 2. Principal component analysis scores of 149 fruit puree HATR spectra, considered in absorbance, in the region 800–2000 cm^{-1}.

frozen or whether it was ripe or underripe. For the strawberry and raspberry purees, these analyses were carried out with the purees produced with self-picked fruits. The procedure used a 59 × 311 matrix for the strawberry purees, a 40 × 311 matrix for the raspberry purees, and a 39 × 311 matrix for the apple purees. Recognition ability only was investigated.

3. RESULTS AND DISCUSSION

3.1. Spectra. Typical spectra of fruit purees are given in Figure 1. As strawberry, raspberry, and apple contain the same major solid constituents (carbohydrates and small amounts of protein and lipids), the spectra are broadly similar. However, some clear differences, particularly in relative intensities, can be observed, but a classification "by eye" is clearly not reliable. Most of the information exists in the "fingerprint region", 800–2000 cm^{-1}, which was used in the data analysis. This region contains absorptions arising largely from pectins, with the carbonyl group stretching appearing around 1730 cm^{-1}, when the acid group of the galacturonic acid is esterified with methanol, and around 1600 (asymmetric) and 1420 cm^{-1}(symmetric). when it is not esterified. In the 1000–1250 cm^{-1} region peaks arise from C–O modes of the carbohydrates.

Table 3. Classification Success Rate (Percent) on a Calibration Set of 149 Spectra of Fruit Purees According to Three Types of Fruits (Strawberry, Raspberry, Apple)

no. of PCs	single beam (%)		absorbance (%)	
	no normalization	area normalization	no normalization	area normalization
7	96.6	97.3	95.9	100
9	96.6	98.6	96.6	100
11	98.6	99.3	98.6	100

3.2. Data Analysis. *3.2.1. Classification According to Fruit Type.* The first series of PCA performed gave some visual evidence of the ability of FTIR to discriminate for fruit type. Figure 2 depicts the scores of the first and third principal components (PCs) of a calibration set containing 149 spectra of strawberry, raspberry, and apple purees. Grouping according to the three fruit types is apparent, and if it were possible to look at more than two dimensions, the very few overlaps that appear would be resolved. It should be noted that all points correspond to physically different samples, and therefore these samples cover a wide range in terms of variety, time of harvesting, and ripeness. However, these factors seem to introduce a variability in the data set, which is not as important as the variability arising from the fruit species. PCA therefore gave a good visualization of this differentiation, as well as reduced the dimensionality of the data to perform a DA. This allowed the quantification of the success with which the fruit purees could be reclassified. This procedure was carried out under several different conditions; the data were first processed as single-beam spectra and then as absorbance spectra, with both cases being analyzed with and without an area normalization of the spectra prior to the PCA. The results obtained for the DA are presented in Table 3. The recognition ability of this method appeared to be extremely good in all cases, with a minimum of 96% success when seven PCs were considered. The results tended to be slightly better after the data set was normalized and when absorbance spectra rather than single beams were used.

The results of the calibration validation procedure are given in Table 4 and show the average of the results for the seven subsets calibration. The success of the calibration process was similar to that of the full set, as expected. The validation procedure also gave extremely good results, with a minimum success rate of 95%. Again, we can observe that using absorbance spectra and normalizing them prior to analysis improved the results considerably.

3.2.2. Detection of Other Characteristics. The ability of DA to discriminate fruit purees according to whether they were from fresh or freeze–thawed fruits was also investigated. For this, the fruit types were considered

Table 4. Average of the Classification Success Rate (Percent) for HATR Spectra of Fruit Purees According to Three Fruit Types (Strawberry, Raspberry, Apple) for Calibration and Validation Sets Using a Cross-Validation Procedure

	no. of PCs	single beam (%)		absorbance (%)	
		no normalization	area normalization	no normalization	area normalization
calibration	7	96.5	97.4	95.6	99.2
	9	96.7	98.8	96.5	100
	11	99.2	99.3	99.3	100
validation	7	95.2	97.2	94.5	97.9
	9	95.9	97.9	96	100
	11	98.6	99.3	98.1	100

Table 5. Classification Success Rate (Percent) of Calibration Sets of HATR Spectra of 59 Strawberry and 40 Raspberry Purees into Purees from Fresh or from Freeze–Thawed Fruits

		single beam (%)		absorbance (%)	
	no. of PCs	no normalization	area normalization	no normalization	area normalization
strawberry	1	98.3	54.2	58.3	66.7
	2	100	94.9	61.7	66.7
	5	100	94.9	71.7	73.3
raspberry	1	75	45	55	52.5
	2	77.5	80	47.5	65
	5	100	100	77.5	87.5

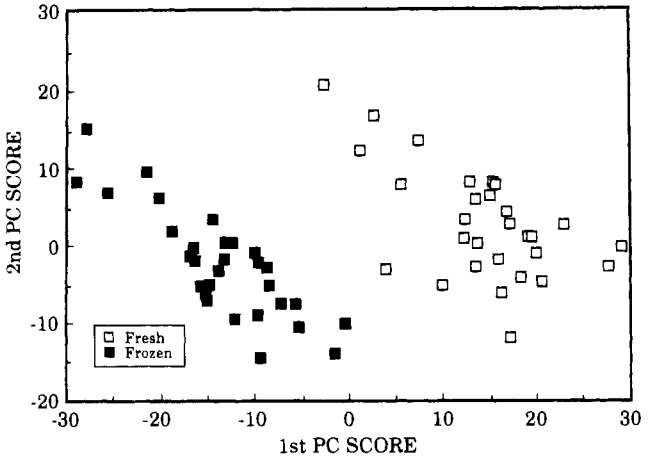

Figure 3. Principal component analysis scores of 59 picked strawberry puree HATR spectra, considered as single beam, in the region 800–2000 cm^{-1}.

individually. PCA was first performed on each data matrix. A plot of the first two PC scores for strawberry purees is shown in Figure 3. In this analysis, the first two PCs accounted for 97.2% of the total variance and entirely explained the characteristic "fresh or freeze–thawed". A DA performed on these PC scores gave 100% success of reclassification with two PCs used. This analysis was performed for both strawberry and raspberry purees, and, again, the same various data treatments were used. Table 5 summarizes the main results. The best classification was obtained when using single-beam, non-normalized spectra. Under these conditions, a DA using only the first PC score correctly reclassified 98.3% of the strawberry purees and 75% of the raspberry purees. The first PC mainly counts for the characteristic fresh or freeze–thawed of the fruit used. Normalizing the single-beam spectra greatly affected these performances, giving less reliable results. However, PC score plots as well as DA results revealed that under these conditions the second PC largely accounted for the variation arising from the fruit being fresh or freeze–thawed.

For strawberry and raspberry purees, the ability to detect whether the fruit used was ripe or underripe was also investigated, again with various data treatments. For the strawberry purees, the results ranged from 50 to 68% success according to the treatment and the number of PCs used. However, results were better with raspberry purees, reaching 92.5% success with six PCs used. The different data treatments did not lead to drastic changes, and no particular trend could be defined. The poorer results could be explained by the fact that the ripeness of the fruit is more subjective.

For the apple purees, several parameters were studied; the analysis distinguished well (about 90% success using one PC) whether the puree had SO_2 added or not. A good differentiation was also achieved between Bramley and other varieties, with about 86% success using two PCs. However, the distinction between purees prepared from pulp only and from pulp and peel was poorer. It has to be noted that for these analyses the sizes of the groups were rather inequitable, with some only containing a few samples.

3.3. Conclusions. The use of FTIR, HATR, and DA classified, with 100% success, fruit purees of three different fruit species, both for a calibration procedure and for an independent data set validation. This method offers a way to classify pure samples very rapidly. In the future, the data base will be increased to include yearly variations. The final objective is not only to classify pure products but also to detect and if possible quantify adulteration. One possibility is the determination of an ellipsoid around each cluster of purees, defining "normal products", as described by Shah and Gemperline (1989). Adulterated products would be expected to arise outside this ellipsoid. The same method also allowed the detection of various characters concerning the purees, such as whether the fruits were fresh or freeze–thawed.

ABBREVIATIONS USED

ATR, attenuated total reflectance; DA, discriminant analysis; EDTA, ethylenediaminetetraacetic acid; FTIR, Fourier transform infrared spectroscopy; HATR, horizontal attenuated total reflectance; HPLC, high-pressure liquid chromatography; PC, principal component; PCA, principal component analysis; SO_2, sulfur dioxide.

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