Food Chemistry 47 (1993) 303–308
Analytical Methods Section

Determination of the fruit content of jam using Fourier Transform Infrared Spectroscopy

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(Received 16 September 1992; accepted 2 November 1992)

An investigation into the potential of Fourier transform infrared spectroscopy for the determination of the fruit content of jam is reported. A quantitative method was developed using dried jam and the potassium bromide pellet technique, in combination with simple linear regression and partial least squares (PLS) analysis. The PLS method gave the best results and showed that the determination of fruit content is feasible in strawberry jam.

A second method, using diffuse reflectance of jam solids washed on filter papers, produced spectra of unusual appearance, but was able to distinguish reproducibly between jams of differing fruit content. Therefore, such a method has potential for the verification of product authenticity and the detection of adulteration.

INTRODUCTION

Consumers are making increasing demands for foods which they consider as wholesome, safe and of high quality. Aspects of safety and quality are regulated and strict labelling requirements exist to protect the consumer. Jams and preserves are examples where the overall fruit content describes what the material is and limits what the consumer will pay. In the UK, strawberry jam must contain a minimum of 35% w/w of fruit and 'extra' jam must have at least 45%. Each product must also bear the declaration 'Prepared with x g of fruit per 100 g,' where x represents the weight of the fruit in question (Anon., 1981). However, the analytical determination of fruit content is extremely difficult, requiring tedious and lengthy wet chemical methods. Indeed, even the definition of fruit content is difficult since there can be considerable variation in, for example, the water content of fruit from different sources. Although unlikely in current commercial practice, it is theoretically possible to substitute part of the required fruit content with cheaper vegetable material. Rapid, reliable detection of such adulteration does not currently exist. What is required is a method of analysis that can be used to define and quantify fruit content and detect adulteration. Of the many new developments in spectroscopy, perhaps the most important for the food industry is Fourier Transform Infrared (FTIR) Spectroscopy operating in the mid-infrared region (Wilson, 1990) which offers tremendous potential for quantitative and qualitative food analysis. The object of this work was to explore the use of FTIR spectroscopy for the quantification of the fruit content of jams and the detection of adulteration. The methods of sample presentation most suited to this type of application are attenuated total reflectance (ATR), diffuse reflectance (DRIFT) and transmission (Belton & Wilson, 1990).

EXPERIMENTAL

All spectra were acquired on a Bio-Rad FTS60 spectrometer at 8 wavenumbers resolution using 256 scans and a deuterated triglycine sulphate detector.

In the first part of the study a range of strawberry jams were prepared containing fruit (frozen strawberry, var. Cambridge Favourite), sugar, glucose syrup, pectin solution, citric acid solution, water and antifoaming agent. In the sample matrix all components were allowed to vary (Table 1). The samples were produced in a way that reflected, as closely as possible, commercial practice.

For samples below 60% fruit content glucose syrup (when added), sugar (when added), antifoaming agent and fruit were mixed together and heated at 25 psi until all ingredients were dissolved and the fruit was soft. Water was added and the mixture boiled at 20–25 psi for 12–15 min until the desired total solids content was achieved. Pectin and citric acid were added and the mixture boiled for a further 3–5 min until the final total solids content was again achieved. The jam was cooled to approximately 85°C and placed into jars. Full jars

Table 1. Matrix used for the preparation of samples

Code	Pectin	Citric	Fruit	Glucose	Sugar	Total Solids	Final Weight	Solid total (%)	Fruit (%)	Soluble Solids (%)
1	0·584	0·027	2·500	1·207	3·078	4·447	6·85	64·9	36·5	64·9
9	0·646	0·027	2·500	1·207	1·777	3·160	6·85	46·1	36·5	46·1
10	0·584	0·029	2·500	1·207	1·777	3·147	6·85	45·9	36·5	45·9
2	0·646	0·029	2·500	1·207	3·078	4·463	6·85	65·2	36·5	65·2
11	0·584	0·027	3·500	1·207	1·777	3·245	6·85	47·4	51·1	47·4
3	0·646	0·027	3·500	1·207	3·078	4·561	6·85	66·6	51·1	66·6
4	0·584	0·029	3·500	1·207	3·078	4·548	6·85	66·4	51·1	66·4
18	0·646	0·029	3·500	1·207	1·777	3·261	6·85	47·6	51·1	47·6
19	0·584	0·027	2·500	2·091	1·777	3·853	6·85	56·2	36·5	56·2
5	0·646	0·027	2·500	2·091	3·078	5·168	6·85	75·5	36·5	75·5
6	0·584	0·029	2·500	2·091	3·078	5·155	6·85	75·3	36·5	75·3
20	0·646	0·029	2·500	2·091	1·777	3·839	6·85	56·5	36·5	56·5
21	0·584	0·027	3·500	2·091	3·078	5·254	6·85	76·7	51·1	76·7
22	0·646	0·027	3·500	2·091	1·777	3·967	6·85	57·9	51·1	57·9
23	0·584	0·029	3·500	2·091	1·777	3·954	6·85	57·7	51·1	57·7
24	0·646	0·029	3·500	2·091	3·078	5·270	6·85	76·9	51·1	76·9
25	0·553	0·028	3·000	1·708	2·514	4·325	6·85	63·1	43·8	63·1
26	0·676	0·028	3·000	1·708	2·514	4·324	6·85	63·6	43·8	63·6
27	0·615	0·025	3·000	1·708	2·514	4·338	6·85	63·3	43·8	63·3
28	0·615	0·031	3·000	1·708	2·514	4·341	6·85	63·4	43·8	63·4
29	0·615	0·028	2·000	1·708	2·514	4·240	6·85	61·9	29·2	61·9
30	0·615	0·028	4·000	1·708	2·514	4·240	6·85	64·8	58·4	64·8
8	0·615	0·028	3·000	0·000	2·514	3·974	6·85	43·4	43·8	43·4
31	0·615	0·028	3·000	2·415	2·514	4·906	6·85	71·6	43·8	71·6
7	0·615	0·028	3·000	1·708	0·000	1·826	6·85	26·7	43·8	26·7
32	0·615	0·028	3·000	1·708	3·555	5·381	6·85	78·6	43·8	78·6
12	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4
13	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4
14	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4
15	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4
16	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4
17	0·615	0·028	3·000	1·708	2·514	4·340	6·85	63·4	43·8	63·4

were then capped and sterilised. For samples above 60% fruit content glucose syrup, sugar, antifoaming agent and water were mixed and boiled at 20–25 psi for 5 min and then the fruit was added gradually with stirring until the fruit became soft. After this the process was the same as for samples below 60% fruit content.

Subsequently, the jams were analysed for total soluble solids using a refractometric method, values being expressed with reference to sucrose. Total solids were determined by vacuum oven drying (Hughes & Maunsell, 1934). Water content was determined from the total solids method and insoluble solids were also measured (ISO, 1981). The sucrose, glucose and fructose concentrations were determined using Dionex ion chromatography. The fruit content of the jams was calculated from the following expression:

$$\text{Corrected fruit content} = \frac{\text{(measured total solids)}}{\text{(predicted total solids)}} \times \text{(predicted fruit content)}$$

Residues on filter paper disc from the insoluble determinations were kept for spectroscopic examination.

Before spectroscopic examination all jams were homogenised on an Ultra Turrax homogeniser for 1 min. Samples of intact jam were applied to a horizontal ATR accessory (Spectra-Tech Europe, Inc.) equipped with a 45° zinc selenide element. Samples were spread directly onto the ATR plate. Unfortunately, the spectra produced were so dominated by water peaks present that very little information could be extracted, even after digital subtraction of the water bands. It was decided that any analytical approach would require the removal of water and the analysis of solid samples. The method chosen was the potassium bromide pellet technique.

For sample preparation, jams were spread thinly on glass plates and dried in a vacuum oven at 50°C for 3 h. The water content of the jam was measured by sample weight loss during the drying procedure. The dry sample was ground in a mortar and sieved. About 0·005 g (± 0·0001 g) of the dry sample and about 0·5 g (± 0·0001 g) of potassium bromide (BDH IR grade) were ground in a mortar. About 0·035 g of the mixture was added to a pellet die (13 mm, Specac Ltd) and pressed under 10 tonnes for 10 min under vacuum.

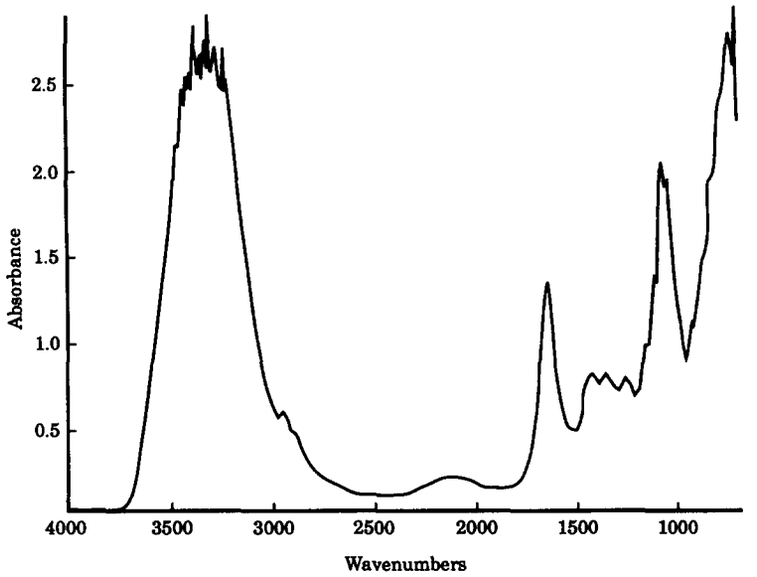

Fig. 1. ATR Spectrum of strawberry jam, illustrating domination by water bands centred at 3600 and 1650 cm^{-1}.

Spectra were then recorded on the Bio-Rad spectrometer using a potassium bromide disc for background correction. The best quantitative results were obtained by plotting the area of a band at 1725 cm^{-1} against the percentage weight of jam in the disc: the latter was calculated from the known mass of dried jam in the disc, the solids content of the jam, the fruit content of the jam and the total disc weight. It was possible to examine six samples per day using this method. Consequently, the final calibration was composed of about five days' individual sub-set calibrations.

Diffuse reflectance (DRIFT) spectra were obtained from the dried strawberry jam samples as well as from other commercially available apricot, raspberry, plum and bramble jams. All jams were dissolved in water (20g per 100 g) and filtered through Whatman No. 1 papers. The papers were washed with 3 × 50 ml volumes of water and dried in an oven, 5 mm diameter were randomly cut from the filter papers and DRIFT spectra were acquired using a Spectra-Tech 'Collector' accessory on the Bio-Rad FTS60. A plain paper was used as the background and spectra were presented in Kubelka–Munk units.

In a second experiment several commercial jams exhibiting a range of declared fruit contents were purchased. These jams were treated in a similar manner but improvements were made to the potassium bromide pellet technique. Sample grinding, disc preparation and storage were carried out in a dry atmosphere to prevent water absorption. All discs were prepared on separate days but all spectra were acquired on the same day; samples were re-dried after grinding and sieving and approximately 25 mg of sample was mixed with 500 mg of potassium bromide. A 200 mg sample of this mixture was used for disc pressing. Duplicate discs were prepared.

Partial least squares (PLS) quantitative analysis was also carried out on the commercial samples. The pack-

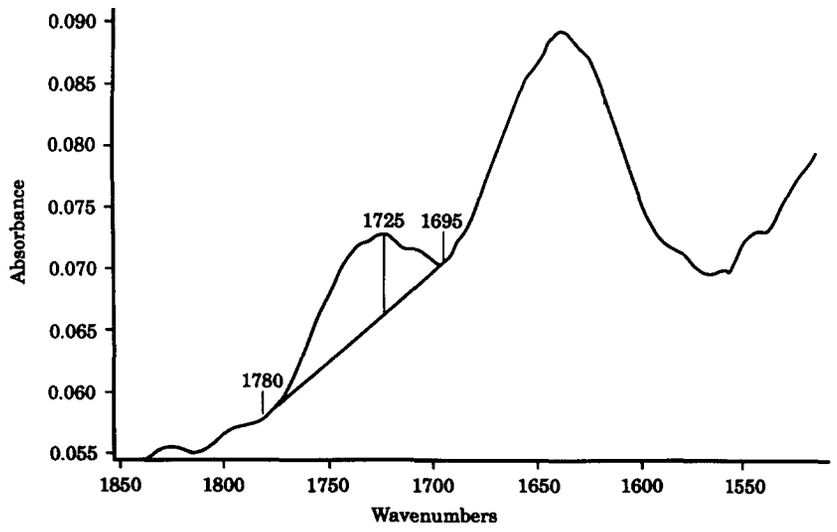

Fig. 2. Potassium bromide pellet spectrum of dried jam samples, showing the peak used for analysis and the baseline used for peak area determination.

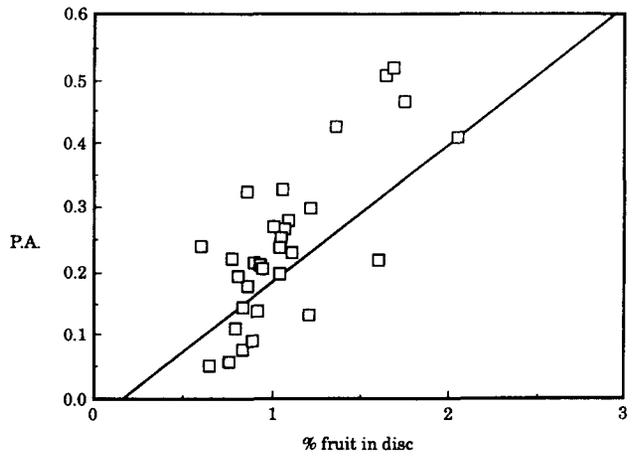

Fig. 3. Plot of area of peak at 1725 cm^{-1} versus fruit content of disc for strawberry jam samples prepared in laboratory.

age used was the Bio-Rad implementation of the PLS2 (Martens & Naes, 1989) algorithm. The samples were divided into a calibration set and a validation set with a replicate of each sample used as either a calibration or validation sample. The spectral range was limited to 1900–1200 cm^{-1} because outside this range the spectra showed evidence of over-absorption resulting from the sample loading used in the disc. The number of factors used (Rank) in the analysis was optimised at five.

RESULTS AND DISCUSSION

The ATR method is attractive since it offers easy sampling for intact samples, but the domination of the water signals limits its applicability (Fig. 1). Results from the potassium bromide pellet technique showed the most useful band for quantification to be at 1725 cm^{-1}. The band is severely overlapped by water in the ATR spectrum and cannot be reliability measured even after subtraction of the water peak.

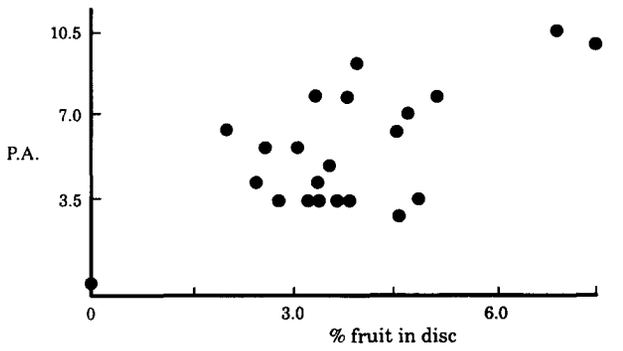

Fig. 4. Plot of area of peak at 1725 cm^{-1} versus fruit content of disc calculated from the declared value of commercial jam samples.

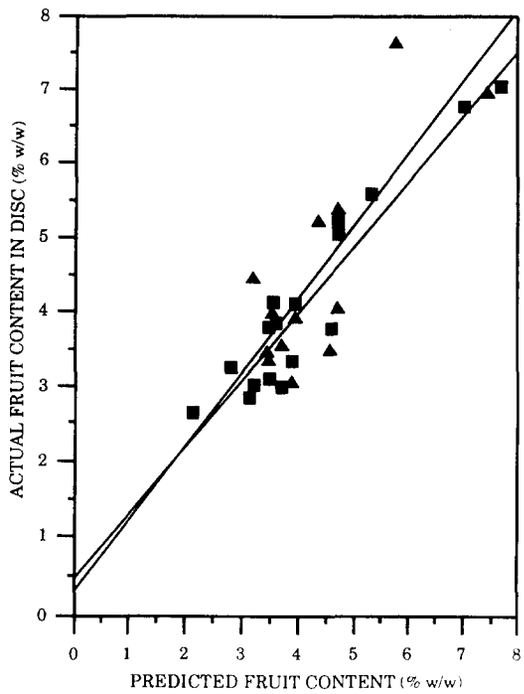

Fig. 5. Calibration and validation plot of predicted versus expected fruit content of commercial jams calculated using Bio-Rad PLS2: □ calibration; Δ validation.

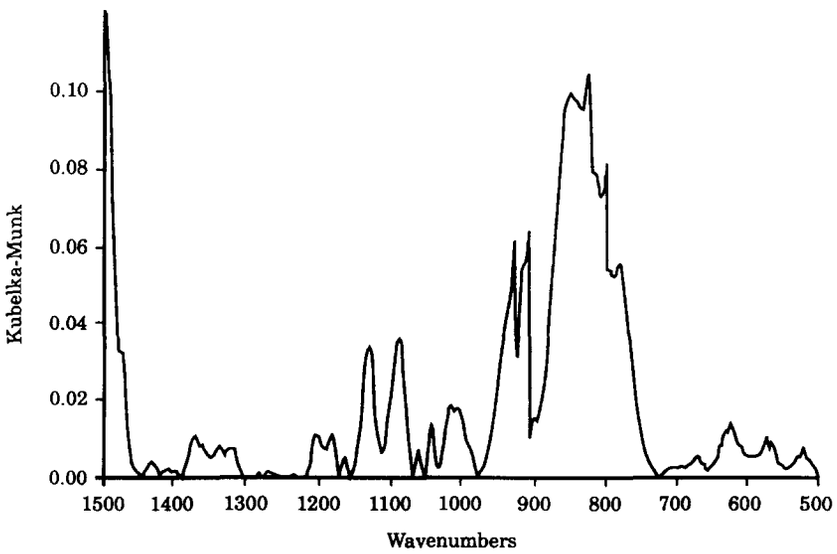

Fig. 6. Diffuse reflectance spectrum of strawberry jam insoluble solids on filter paper.

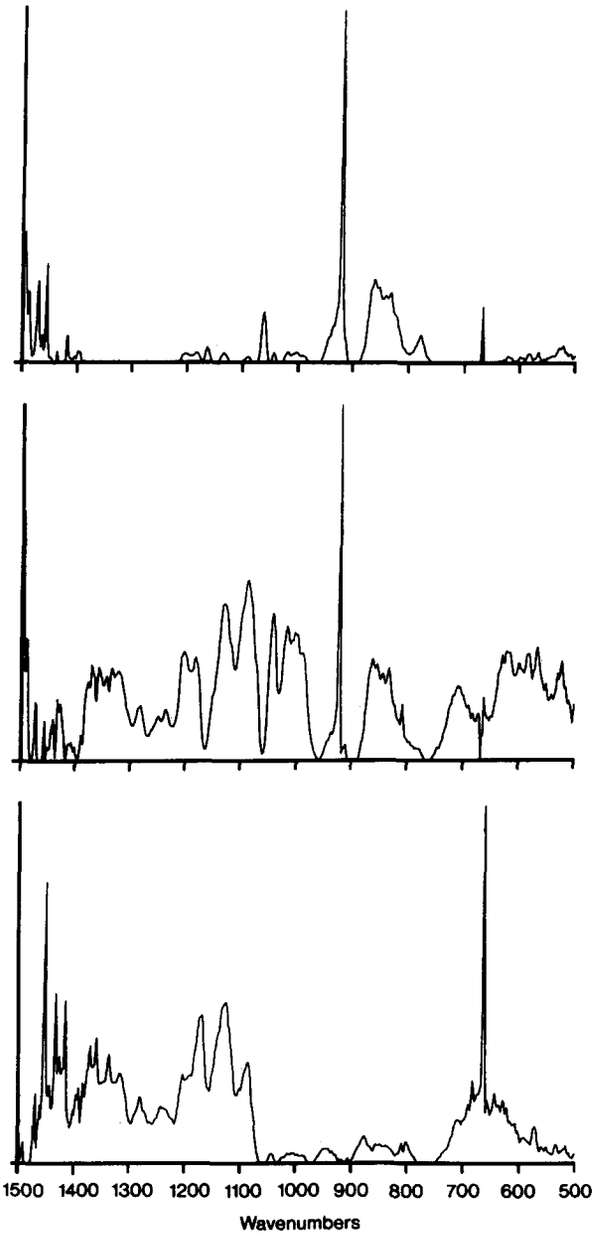

Fig. 7. Diffuse reflectance spectra of various fruit jams on filter paper. Top: raspberry; centre: apricot; bottom: bramble. *Y*-axis is the Kubelka–Munk units.

The 1725 cm^{-1} band used for quantitative analysis with the potassium bromide pellet technique is shown in Fig. 2; it is at a frequency characteristic of ester functionalities, probably arising from the cellular pectin of the strawberry. This band is not affected by added pectin (apple) since no correlation could be made between this peak area and the added pectin content; indeed, any sort of correlation was only achieved against the weight of fruit in the disc (Fig. 3). However, the plot showed a high degree of scatter (correlation coefficient 0·77). An interesting observation was that the correlation coefficients of the sub-sets that were run on any particular day (typically 6–7 samples) were much better (e.g. 0·95). It was also observed that certain samples absorbed water from the atmosphere during preparation after the drying stage. In addition, the concentration of sample in the disc, and indeed the disc thickness, could be increased to improve the signal-to-noise ratio, as the measured band was only of moderate intensity. Improvements were therefore made to the second experiment involving commercial jams. The plot of peak area versus weight of jam in the sample calculated from declared fruit content is shown in Fig. 4. In this experiment a correlation coefficient of 0·55 was achieved (0·67 with a sucrose blank representing zero fruit content).

The calibration generated by selecting six samples (the two concentration extremes plus four random) for preparation and acquisition of data on the same day gave a better correlation coefficient of 0·76.

The PLS results were very encouraging. Without the use of a blank disc (zero fruit content) it was possible to achieve a calibration correlation coefficient of 0·94 (Fig. 5). However, with PLS it is always possible to overfit data and consequently a more reliable indicator of the quality of the calibration is given by the correlation of the validation set. In this case the correlation coefficient was 0·82, which can be considered quite resonable, especially given that some of the samples were not analytically prepared but were obtained commercially and no pathlength correction was applied. A second problem may arise in the sample preparation step. It is known that the apparent absorptivity in transmission spectroscopy is dependent upon the particle size of the sample (Kortum, 1964). In this experiment, the nature of the dried sample is such that it is not possible to control the particle size with any degree of certainty This will clearly affect the quantitative accuracy of the method. However, it is clear that the potassium bromide pellet method combined with PLS has great potential for the estimation of the fruit content of jam.

The result of the diffuse reflectance work for strawberry jams is shown in Fig. 6. Spectra in the region illustrated are not as expected, show considerable distortion, and were not suitable for quantification.

The reasons for the appearance of the diffuse reflectance spectra are complex. Reflection at a surface may be of two types. Where the surface is shiny light is specularly reflected and contains no information about the absorption spectrum of the sample. At scattering surfaces there may be diffuse reflectance where the light enters the sample and may be emitted at any angle. This does carry spectral information, as some of the light has been absorbed by the sample. Most real samples generate a mixture of diffuse and specular radiation and the presence of the specular radiation leads to spectral distortion, usually in the form of 'compressed' spectra (Belton & Wilson, 1990). Strongly absorbing samples in which anomalous dispersion arises may also give rise to derivative shaped peaks. Consequently, the diffuse reflectance spectrum is very sensitive to the nature of the sample, its surface properties, its absorptivity and its refractive index. Nevertheless, the pattern for strawberry was found to be very reproducible. Furthermore, all fruits tested gave rise to characteristic patterns that were also reproducible (Fig. 7). The spectra thus act as fingerprints for different fruit types.

CONCLUSION

The results indicate that there is some potential for the use of FTIR spectroscopy for the analysis of jams and that the potassium bromide pellet technique is most suited for quantitative work. However, there is room for improvement. Much of this work has been based on straightforward Beer-Lambert type calibrations using a limited spectral range. Although this showed promise, the real future potential probably lies with multivariate methods such as PLS.

The DRIFT spectra illustrate another potentially powerful area for FTIR spectroscopy in authentication. Although the spectra are clearly distorted, they are reproducible and can be considered as 'fingerprints'. In practice, therefore, the situation can be envisaged where the pellet technique is used to quantify the fruit content and the DRIFT method confirms the fruit type and detects adulteration.

In conclusion, these results show that FTIR spectroscopy can be used to determine fruit content in jams and can provide confidence as to their authenticity, thus opening up many new possibilities for FTIR spectroscopy in food technology.

ACKNOWLEDGEMENT

The authors wish to thank the Ministry of Agriculture, Fisheries and Food for sponsoring this work.

REFERENCES

Anon. (1981). *The Jam and Similar Products Regulations.* SI 1981, No. 1063, HMSO, London.

Belton, P. S. & Wilson, R. H. (1990). Infrared sampling methods. In *Perspectives in Modern Chemical Spectroscopy*, ed. D. L. Andrews. Springer-Verlag, Berlin.

Hughes, E. B. & Maunsell, A. E. (1934). The analysis of fruit and fruit products. *The Analyst*, **59**, 231.

International Standards Organisation: 751 (1981). *Fruit and Vegetable Products—Determination of Water Insoluble Solids.* First edition, 10–15.

Kortum, G. (1964). *Reflectance Spectroscopy.* Springer-Verlag, Berlin and Heidelberg.

Martens, H. & Naes, T. (1989). *Multivariate Calibration.* Wiley, Chichester, UK.

Wilson, R. H. (1990). Fourier transform infrared spectroscopy for food analysis. *Trends in Analytical Chemistry*, **9**(4), 127–31.