

## Recent Developments in Food Characterization and Adulteration Detection: Technique-Oriented Perspectives

CHRISTOPHE CORDELLA,<sup>\*,†,‡</sup> ISSAM MOUSSA,<sup>§</sup> ANNE-CLAIRE MARTEL,<sup>†</sup>  
 NICOLAS SBIRRAZZUOLI,<sup>#</sup> AND LOUISETTE LIZZANI-CUVELIER<sup>‡</sup>

Agence Française de Sécurité Sanitaire des Aliments (AFSSA), Unité Abeille, B.P. 111, F-06902 Sophia-Antipolis Cedex, France;  
 Université de Montpellier II, ISEM UMR 5554, cc064 Place E. Bataillon, F-34095 Montpellier Cedex 5, France;  
 Laboratoire de Thermodynamique Expérimentale, CNRS UMR 6595, Parc Valrose, F-06108 Nice Cedex 2, France; and  
 Laboratoire Arômes Synthèses Interactions, Université de Nice Sophia-Antipolis, Parc Valrose, F-06108 Nice Cedex 02, France

This review covers mainly publications that appeared in *Analytical Abstracts* (Royal Society of Chemistry) from January 1990 to February 2001. The number of publications on this topic continues to grow, and during the past three years (1998–2000) about 150 reviews and/or overviews have been published in the area of food. Numerous techniques and food matrices or chemical components are presented and discussed in these reviews. The present review is intentionally limited to eight techniques or classes of techniques and intends to be a “technique by technique” presentation of “what was used” or “what is used” to characterize food products and to detect their possible adulteration. The present review focuses on the following techniques: microscopic analysis; HPLC; GC, GC-(MS, FTIR); UV–visible spectrophotometry; AAS/AES, ICP-(AES, MS); IRMS, GC-IRMS, GC-C-IRMS; DSC; IR, mid-IR, and NMR (202 references). Emphasis is placed as much as possible on chemometrical treatment of analytical data, which are commonly used to achieve the final objective, either food characterization or adulteration detection. Finally, a brief description is given of the new generation of analytical systems that combine powerful analytical techniques and powerful computer software for a best extraction of the information from analytical data.

**Keywords:** Microscopy; HPLC; GC; MS; GC-FTIR; AAS; AES; ICP-AES; IRMS; DSC; IR; NMR; SNIF-NMR; HPIC-PAD; chemometrics; ANN; food characterization; food adulteration

### INTRODUCTION

This review covers mainly publications that appeared in *Analytical Abstracts* (Royal Society of Chemistry) from January 1990 to February 2001. However, some older papers are also included to illustrate some historical aspects. The number of publications on this topic continues to grow, so some important contributions have certainly been omitted, for which we must apologize. For the past three years (1998–2000) about 150 reviews and/or overviews have been published in the area of food science. Numerous techniques and food matrices or chemical components are presented and discussed in these reviews. This review is therefore intentionally limited to eight techniques or classes of techniques and offers a “technique by technique” presentation of “what was used” or “what is used” to characterize food products and to detect their eventual adulteration. For a food matrix oriented presentation, see the paper published by Dennis (*1*). For further information related to each technique presented here and their recent developments

in food science (from Jan 1998 to Dec 2000), the reader will find some additional bibliography resources at the end of this review (**Tables 6 and 7**).

Frauds in various consumer sectors are now commonly practiced. Raw materials the farm-produce sector are not exempt, and according to the activity report of the French General Directorate for Fair Trading, Consumer Affairs and Fraud Control (DGCCRF) (*2*), this practice is increasing. Authentication of food products is of primary importance for both consumers and industries, at all levels of the production process, from raw materials to finished products. From the legislative point of view, quality standards have been established through the requirement of quality labels that specify the chemical composition of each product. From the economic point of view, product authentication is essential to avoid unfair competition that can create a destabilized market and disrupt the regional economy and even the national economy. All food products targeted for adulteration are high-commercial-value products and/or produced in high tonnage around the world. **Table 1** assembles products having the potential to be adulterated, adulteration modes, and techniques used for their detection. For example, Briandet et al. (*3*) reported that two types of adulteration could be used in coffee: adulteration with substitutes such

\* Author to whom correspondence should be addressed (fax 33 4 92 94 37 01; e-mail c.cordella@sophia.afssa.fr).

† Agence Française de Sécurité Sanitaire des Aliments.

‡ Université de Nice Sophia-Antipolis.

§ Université de Montpellier II.

# Laboratoire de Thermodynamique Expérimentale.

**Table 1.** Common Types of Food Adulteration (Courtesy of Eurofins Scientific Analytics)

product	common adulteration	common detection method
aloe vera gel	dilution	compositional parameters
berry jam	addition of cheaper berries	HPLC
fruit juice	addition of or dilution with water	<sup>9</sup> Brix, (D/H), and <sup>18</sup> O IRMS
fruit juice	addition of sugar	gas chromatography, <sup>13</sup> C IRMS, and SNIF-NMR
honey	addition of corn or cane sugar	<sup>13</sup> C IRMS
meat	addition of cheaper meat	molecular biology methods
milk	species of origin	electrophoresis, immunoassay
natural aroma	addition of non-natural aroma	chiral chromatography
natural vanilla extract	addition of artificial vanillin or <i>p</i> -hydroxybenzaldehyde	<sup>13</sup> C IRMS and SNIF-NMR
soy	genetic modification (in the EU)	DNA methods
spirit	mislabeling of botanical origin	<sup>13</sup> C IRMS and SNIF-NMR
St. John's wort	replacement by other herbs	chromatography
vegetable oil	addition of cheaper seed oil	chromatography and mass spectrometry
wine	dilution with water	(D/H) and <sup>18</sup> O IRMS
wine	chaptalization	<sup>13</sup> C IRMS and SNIF-NMR
wine and spirit	mislabeling of age	<sup>14</sup> C scintillation counting

as chicory, malt, cereals, caramel, maltodextrin, and glucose, and adulteration by mixing two coffee qualities (addition of a less expensive robusta coffee to an arabica coffee and sold under “pure arabica” designation). The latter practice is also applied to other common food products such as wine, fruit juice, olive oil, butter, and honey.

The detection of adulteration is a technical problem. Indeed, we must wonder about the following question: How can we detect an adulterant having approximately the same chemical composition of the food product in which it is included?

The first approach consists of determining the ratio between some chemical constituents and assumes these ratios are a constant component of the particular food. From this point of view, it seems to make sense that any addition of any substance(s) into foods will modify the value of these ratios or will highlight an anomaly in its chemical composition. This approach is frequently associated with a large set of analyses and the use of chemometrics. In this area, many pattern classification procedures (such as PCA, LDA, HCA, SIMCA, PLS, CVA, and ANN) can be applied to the dataset to compare similarities or differences of sample data with original data. Theoretically, after a multivariate analysis taking into account many analytical factors, adulterated samples form singular groups that can be easily distinguishable from authentic samples.

An alternative approach to this problem could be to search for a specific marker in the product, which could be a chemical constituent (complexes, molecules, nucleic acids) or morphological component (plant cells), that proves either the adulteration or authenticity of the food.

The third possibility for detection of adulteration in foods is the global approach of the food products. The method consists of using analytical techniques derived from physical analysis by considering the whole of the sample to show the effects of the adulteration on the physicochemical properties of the sample. Rather than measuring one chemical parameter such as pH, conductivity, water content, pt ash content, a physical analysis, such as thermal analysis (TGA + DSC), observes the thermal behavior of the food. The thermal behavior is followed over changing temperature and/or time.

To carry out these analytical controls, many techniques are used and/or usable. This review focuses on the following: microscopic analysis; HPLC; GC, GC-MS, GC-FTIR; UV-visible spectrophotometry; AAS/AES, ICP-AES, ICP-MS; IRMS, GC-IRMS, GC-C-IRMS; DSC; and IR and mid-IR, NMR.

The final goal can be either food characterization or adulteration detection.

## MICROSCOPIC ANALYSIS

Optic or electronic microscopic analyses are not very applicable techniques in the food area except for honeys, for which they are very useful. The first studies relating to the use of optical microscopic analysis as a characterization tool of the floral origin of honey appeared in the 1950s when Maurizio (4) described a quantitative study of pollens in honeys. Louveaux and Maurizio (5) used optical microscopic analysis to characterize European melliferous plants by establishing their “pollinic identity card”. The following year, Louveaux (6) applied this technique with success to 40 Canadian honeys. In 1978, Louveaux and Maurizio (7) published “Methods of Mellissopalynology”, which has since become the official method for determining honey floral origin. Since 1978, numerous honey characterization studies have been published using palynology to distinguish among honeys from various countries. Now, analysts prefer to combine microscopic analysis with physicochemical determinations to determine floral origin of honeys. This practice is used increasingly as seen in Cortopassi-Laurino et al. (8) to study bactericide effects of some Brazilian honeys and in Thrasyvoulou et al. (9) in Greek monofloral honeys. Recently, Kerkvliet et al. (10, 11) applied the Louveaux–Maurizio method to the preparation of the samples and to the detection of adulteration of honeys with cane sugar and cane sugar products using optical microscopy. This study is based on the detection of parenchyma cells, sclerous rings, and other cane sugar constitutive cells. The latest review about analytical methods to determine the geographical and botanical origin of honeys and for proving their authenticity was published by Anklam et al. (12).

With the appearance of scanning electron microscopy (SEM), the development of palynology reached a turning point in the 1980s. With certain floral species, it is impossible to highlight, on live preparations, differences in hexin structure. This problem is linked to the weak field depth of optical microscopes. Using electron microscopy, this limitation is overcome and the determination of the botanical origin of honeys having similar palynologies is now possible without ambiguity.

In this area, several works should be emphasized, particularly, the work of Dustmann et al. (13–15), where SEM was used to describe the surface pattern of pollen from honeys. In the same way, Ohe et al. (16) used SEM to study pollen from apple varieties. Despite improvements brought about by SEM, electronic microscopic analysis is not a cheap routine technique, and it requires a meticulous sample preparation. When identification of pollens from a “fresh-state” is not possible, the

**Table 2.** Main Analyses Carried out on Honeys for 25 Years by HPLC

analyzed compounds	aim of study	year (ref)
amino acids and sugars	storage effects on honey chemical composition and properties	1976 (130)
sugars	determination of oligosaccharides origin	1988 (137)
amino acids	floral origin and/or geographical determinations	1975 (132, 133) 1989 (134)
flavonoids		1989 (135)
sugars		1990 (136)
phenolic compounds		1997 (137) 2000 (138)
amino acids enantiomers		1994 (139, 140)
sugars and conductivity		1996 (141)
organic acids		1998 (142)
sugars, amino acids, HMF, glucosidases, yeast, free acids, diastase, lactone, ash	floral characterization and chemical composition	1992 (143)
organic acids	chemical composition	1994 (144)
sugars	determination of honey authenticity	1994 (136)
HMF	HMF determination methodology	1996 (145)
abscissic acid	marker research into a floral species	1996 (146)
pyrrolizidine-derived compounds	sensibility improvements for alkaloid compound determination in honeys	1997 (147)
flavonoids	chemical composition	1997 (148)
kaempferol	determination of flavonoid origin	1998 (149)

preferred technique is Erdtman's, which consists of observing pollens after sample acetolysis (17).

### HPLC

High-performance liquid chromatography is one of the most widely used techniques in analytical chemistry. In an industrial or laboratory setting, HPLC represents one of a series of control and research tools routinely employed.

In the farm-produce industry, HPLC is used as a quality control tool because it can separate various chemical constituents of mixtures, but it is also often used for characterizing food products or to detect adulteration. Blanch et al. (18) proposed various approaches to evaluate the authenticity of olive oil and hazelnut oil by HPLC and HPLC-GC. This work of characterization is based on the hazelnut oil marker [filbertone: (*E*)-5-methylhept-2-en-4-one], being absent in olive oil, which allows the detection of olive oil adulteration (19). Similarly, Silva et al. (20) uses the specific phenolic compound profile present in commercial quince jams to detect adulteration of quince jams by pear or apple purée. After determining that the phenolic profiles are similar, they used reversed-phase HPIC-PAD method to find a specific marker of pear purée (arbutin), proving the fraudulent adulteration of analyzed samples. Mouly et al. (21) proposed a simultaneous method to determine flavone glycosides and polymethoxylated flavones in citrus juices such as orange and lemon juices. Guyot et al. (22) analyzed phenolic compounds in various French ciders, whereas Bengoechea et al. (23) made the same analyses on manufactured purées and concentrates from peach and apple fruits. The previous examples illustrate the second approach consisting of the identification of a specific marker of the natural food product or the marker belonging to the adulterant. The third approach can be illustrated in the application of HPLC data in the classification of cheese varieties by multivariate analysis of HPLC profiles as shown by Mohler-Smith et al. (24). They applied both principal component analysis and linear discriminant analysis to 55 peak areas from each cheese chromatogram, with >90% correctly classified. The utilization of linear discriminant analysis after principal component analysis improves the classification of the dataset as opposed to the direct utilization of the discriminant analysis.

Numerous chemical compounds are extensively analyzed by HPLC either for species characterization or for authenticity

research: flavonoids in fruit juices (25, 26), organic acids in apple juices (22, 27), phenolic pigments in black tea liquors (28, 29), proline isomers and amino acids in wines (30–32), and anthocyanins in jams (33), juices, etc. HPLC has been very widely used for 25 years for the determination of the chemical constituents of food. Most of the chemical compounds cited previously were also found, analyzed, and studied in honeys either for characterization purposes or for adulteration detection objectives (cf. **Table 2**). The diversity of the compounds mentioned above shows the high complexity of certain food matrices such as honey and other nontransformed natural products.

### GC, GC-FTIR, AND GC-MS

Gas chromatography is used for separating volatile organic compounds. Numerous detectors for this kind of chromatography have been developed since the 1950s, and several of them have high sensitivity and/or selectivity. (For further information about various kinds of chemical detectors such as NPD, ECD, AED, FID, MS, and FTIR, see ref 34). The attraction of hyphenated techniques, such as GC-MS or GC-FTIR, comes from the necessity to determine the identity of separated chemical compounds. The principles of these techniques as well as the working process are described elsewhere (34), but here we will discuss some applications of GC, GC-MS, and GC-FTIR to food products.

The literature seems to show the GC-MS coupling as the most widely used hyphenated technique (>50%). GC comes in second, with ~20% of cases, and third is GC-FTIR (<10%). However, the use of GC-FTIR is increasing because it is a nondestructive technique with respect to the sample. Moreover, GC-FTIR gives some structural information on the chemical functional groups of the molecules (acid, alcohol, amine, aromatic groups, etc.). Gas chromatography is generally used to discriminate among different varieties of the same product, adulteration detection, and organic compound authentication and identification (cf. **Table 3**). GC or GC-MS is frequently used in association with a large set of analyses and with chemometric data treatments. This is an illustration of the second approach (able to detect adulteration and appropriate for characterization) presented in the Introduction of this review. Sivertsen et al. (35) presented a study in which PCA and CVA were applied to evaluate similarities among wines from the same regions and

**Table 3.** Main Studies in Food Area Using Gas Chromatography and Its Couplings for the Past 10 Years

food product	analyzed compounds	technique(s)	aim of study	year (ref)
apricots purée	volatile compounds	GC-MS	characterization and/or classification	1990 (150)
wines	aroma	GC (FID)		1996 (151)
tea	fatty acids and volatile compounds	GC + GC-MS		1998 (152)
orange essential oils	polymethoxyflavones	GC-MS		1998 (153)
wines	volatile compounds	GC + GC-MS (ITD)		1995 (154)
raspberry	aroma	GC-FTIR + GC-MS		1997 (155)
orange juices	lipidic fraction	GC-MS		1998 (156)
honeys	amino acids	CG	geographic origin determination	1981 (157)
	sugars	CG (FID)	floral or botanical origin determination	1995 (158)
	carboxylic acids	CG (FID) + CG-SM		1995 (159)
	norisoprenoids, monoterpenes, and other volatile compounds	CG (capillary) + GC-MS		1997 (160)
	sugars	CG + TLC		1987 (161)
	oligosaccharides	GC + GC-MS		1998 (162)
	amino acids	CG		1992 (163)
	hesperetin and methylanthranilate	CG + HPLC	search of a marker of floral origin	1994 (164)
white wine	volatile compounds	GC-MS	geographic origin	1995 (165)
essential oils	terpenes	GC-MS		1994 (166)
essential oils	linalol, limonene, acetate of linalyl, and related compounds	GC (chiral)	adulteration detection and/or authentication	1997 (167)
European virgin olive oil	volatile and nonvolatile compounds	GC		1997 (168)
green coffee	sterol-derived compounds	GC		1998 (169)
compounded beverages	sterol compounds	GC-MS		1998 (170)
honeys	sugars	CG (capillary)		1995 (171)
blackcurrant	terpenes	HPLC + GC-MS	impact of volatile compounds on taste	1995 (172)
aulx	volatile sulfur compounds	FDP-GC + GC-MS	identification	1998 (173)
cherry	volatile, nonvolatile compounds, sugars, and organic acids	GC-MS	physicochemical properties	1998 (174)
citrus essential oils	fructo-oligosaccharides	GC-MS	detection of chemical contaminants	1999 (175)

the main differences among wines from the different regions. Twenty-one sensory attributes (i.e., color intensity, suppleness, astringency, fruit acidity, etc.) and 35 chemical compounds (i.e., ethanol, ethyl acetate, malic acid, lactic acid, glycerol, isobutanol,  $\gamma$ -butyrolactone, etc.) have been measured to classify 22 red wines. About 82% of samples were correctly classified by the chemical analysis, whereas the classification obtained from the sensory data set was ~64%. Nogueira et al. (36) used PCA and HCA for characterization of commercially available Madeira wines according to different types and ages. Volatile compounds such as 1-propanol, 2-methyl-1-propanol, 2-propen-1-ol, and 3-methyl-1-butanol were measured and quantified by GC or GC-MS, yielding 30 physicochemical parameters usable for pattern classification. After PCA, 14 variables seem to describe adequately the samples according to age, and the first two PCs explain 53% of the variability among all samples studied. To improve the results, the authors employed discriminant analysis, particularly, CVA, to determine which physicochemical variables better discriminate between the type and age groups. Two discriminant functions were obtained explaining 95.5% of the variability, clearly showing a good separation of the overall groups of samples involved. In the same way, König and Schreier (37) describe a PCA/HCA application allowing the selection of aroma constituents of apple juice as key components in the authenticity verification of this product.

A complementary and very powerful tool increasingly used for the characterization of foods is that of artificial neural networks (ANNs), for which the reader may find a vast quantity of information in the scientific literature, the detailed principle of which will not be described here. The main advantage of the utilization of ANNs is that certain classes of ANNs using "supervised learning" tools can learn from sets of chemical data for which the sensory output is known. This is the case of ANNs using an algorithm based on the back-propagation of error. However, ANNs need a large set of data to work, which represents their main disadvantage. Angerosa et al. (38) applied ANN (using back-propagation algorithm) to the olive oil headspace results (input) with the aim of predicting panel test scores (output). A high level of accuracy was found, with ~96%

of answers being correct. This result suggests, according to the authors, that sensory evaluation from the panel test could be successfully replaced by the dynamic headspace analysis-ANN coupled approach.

#### UV-VISIBLE SPECTROPHOTOMETRY

Numerous techniques based on protein structure, peptides, and/or amino acids have been developed to determine the nitrogenous content of food products such as cheese, milk, or honey. They have also been developed to characterize food products containing various kinds of substances such as fatty acids, sugars, vitamins, or mineral elements. Most of these techniques are spectrophotometric or fluorometric methods. Two types of chemical reactions used by these methods can be distinguished:

(1) First are reactions allowing protein or peptide quantification as the Kjeldahl method (IDF standard, 1964) based on the determination of the nitrogen content after a sample mineralization step. Another way is Hull's method (1947) using a complexation reaction of tyrosine with the Folin-Ciocalteu reagent. The complex formed is blue. This method was used again and improved later by Citti et al. (1963) for the determination of nitrogenous compounds in milk. Lowry's method (1951), improved by Creighton (1993), belongs to the most widely used colorimetric methods in analytical chemistry and biochemistry. Based on the biuret reaction, Lowry's method allows for protein and peptide quantification using the complexation reaction occurring between  $\text{Cu}^{2+}$  ions and the Lowry reagent (pH >8). Finally, Soedjak's (39) method has to be highlighted because it is based on the formation of a pink complex, stable for pH <6, between proteins and erythrosine B.

Nowadays, the evaluation of the protein content is mainly based on the Kjeldahl method (seen above) and the Bradford method (40). The method is based on the reaction between Bradford's reagent (Coomassie Brilliant Blue G-250, phosphoric acid, and ethanol) and proteins leading to the formation of a protein-dye complex. A blue coloration is developed in the

spectrophotometric cuvettes in  $\sim 2$  min and is stable for 1 h. The measurement is made at 595 nm. The reliability and the robustness of this method are its main advantages, and this is the principal reason for which Bradford's method is now preferred over other methods. Moreover, this method can be easily automated, and the Bio-Rad firm has developed a version for microtiter plates well adapted to a routine utilization (41). The sensitivity of this variant is suitable for this type of measurements. In addition, this method removes most of the problems involved in the procedures described above (i.e., Lowry's method), which are subject to interference by compounds such as potassium ions, magnesium ions, EDTA, carbohydrates, thiol reagents, and Tris buffer.

(2) On the other hand, specific chemical reactions exist permitting amino acid determinations or amino groups only, such as ninhydrin reagent, used for the first time by Ruhemann in 1910 but modified and improved many times. One of the last applications of this method is published by Wilkinson et al. (42), who utilized the chemical reaction to derivatize amino acid samples in order to inject them in GC determinations.

Ninhydrin normally forms blue complexes with most amino acids, except with those having a tertiary nitrogen, such as proline and hydroxyproline, with which it forms pink complex (43).

The last three methods that are classed in this category are the TNSB (trinitrobenzenesulfonic acid) method, the method using *o*-phthalaldehyde, or, better, that using fluorescamine. The first forms yellow complexes with primary amines, whereas the second, which reacts with  $\alpha$ -amino group of amino acids and short peptides, give a fluorescent compound. The third, using 4-phenylspiro[furan-2(3*H*,1-phthalan)-3,3'-dione] (fluorescamine), reacts quasi-instantaneously with primary amines to give also a fluorescent compound at room temperature. Further details on these various approaches are given by Wallace and Fox (44) for specific cheese and cheese fraction applications.

In the honey area, fluorometric methods were not very widely applied (45–47). On the other hand, spectrophotometric methods have been widely used for about 20 years to make specific analyses of some chemical compounds of honeys. White et al. (48) used UV–visible spectrophotometry to determine the proline content in American honeys, and Davies et al. (49) applied this method for geographical origin determination to distinguish between English and Welsh honeys. In these two cases, the method is based on the ninhydrin reaction to produce colored samples. The most recent spectrophotometric application in the honey area makes use of enzymatic processes for determining various parameters such as glycerol content (50), which can be considered to be an indicator of the fermentation state of honey. D-Gluconic acid (51), galactose, lactose (52), and L-malic acid (53) contents are other honey constituents that can be evaluated by enzymatic methods. All of these methods work as honey characterization tools and together provide a good indication of honey quality.

#### AAS/AES/ICP-AES

Atomic absorption (AAS) or atomic emission (AES) are very old analytical techniques, older than GC or HPLC. AAS/AES use the physical properties of any chemical element that composes the matter, particularly the common possibility for all mineral elements listed in the Mendeleev classification, to absorb or to emit a monochromatic beam with a wavelength specific of each of them. This absorption or emission is considered to be a fingerprint of the particular element being analyzed.

Determination of the mineral content in food products started in the 1930s. In 1932, Shuette et al. were interested by minerals in honeys and highlighted the relationship between the pigmentation degree and the mineral content. Later, McLellan et al. (54) used AAS to measure calcium, magnesium, potassium, and sodium contents in honeys, followed by Petrovic et al. (55), who determined the selenium content from only Eastern Croatia honeys. AAS/AES and ICP-AES are very useful techniques for the mineral content determination of food products (56). More and more applications of these techniques are now available in the literature, particularly applied to wines (57), cheeses (58), sugars (59), and honeys (60–62).

Some studies have been published in recent years concerning detection of the adulteration in food products by AAS/AES, these techniques having been mainly used to make characterizations, as, for example, done by Moussa (63) and Lapiere (64), in determining the geographical origin of honeys. However, recently Simpkins et al. (65) suggested the use of AAS and ICP-AES to detect adulteration of Australian orange juices by showing that many elements are present in various concentrations depending on the origin of the orange juice. By using principal component analysis, the mixing of two qualities of orange juice was verified. Here again, the application of this type of technique in food analysis can require the treatment of a large quantity of data that implies the utilization of chemometric methods. Sun et al. (66) applied both discrimination analytical methods (ACP, HCA, Bayes discrimination method, and Fischer discrimination method) and ANN (back-propagation architecture) methods to ICP-OES (optical emission spectrometry) data to classify wine samples from six different regions. The results obtained by ANN compared with those obtained by conventional Bayes discrimination analysis and Fischer discrimination analysis methods show a satisfactory prediction coefficient (100%), whereas the Bayes method gives a discrimination rate of 98.8% for the prediction set and the Fischer method provides a discrimination rate of 91.8% for the prediction set. However, the ANN approach takes the longest computing time among all of the methods.

#### IRMS

For many years, isotope ratio mass spectrometry (IRMS) has been the official technique to detect adulteration in honey and other food products. The first major work in this area was presented by White and Doner, who proposed a method to detect a potential industrial syrup addition (from C-4 plants) in food products and particularly in honeys (67).

The principle of IRMS is easy to understand. The procedure consists of measuring the isotope ratio of an analyte converted into a simple gas, isotopically representative of the original sample before entering the ion source of an IRMS system. The system performs isotope ratio measurements ( $^2\text{H}/^1\text{H}$ ,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{18}\text{O}/^{16}\text{O}$ , and  $^{34}\text{S}/^{32}\text{S}$ ) continuously on gases of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{SO}_2$ , respectively. For example, in the case of carbon, the  $^{13}\text{C}/^{12}\text{C}$  ratio is naturally constant in all biological products but can fluctuate from one C source to another (atmospheric  $\text{CO}_2$ , C4 plants, C3 plants, animal carbon, etc.), so it is easy to detect whether these different C sources were mixed because the  $^{13}\text{C}/^{12}\text{C}$  ratio of the product will have shifted compared to that of the natural product.

For more theoretical and practical details see the review by Meier-Augenstein (68), who presents all aspects of the IRMS system utilization detailing the sample preparation, derivatization, isotopic calibration, etc., and gives examples of many applications on flavors and fragrances, wine, fruit juice, vegetable oils, and honey with more than 160 references.

**Table 4.** Main Works Realized between 1980 and 2000 by DSC or by DSC Completed by Other Techniques

product or food compounds	aim of study	parameters used	year (ref)
sucrose	study of amorphous sucrose transformation into crystallized sucrose	nucleation time, sucrose granule diameter against time $T^{\circ}$ fusion, $\Delta H$ fusion, van't Hoff eq, Arrhenius eq	1990 (176)
sucrose-containing preparations	stability	$T_g$ , $\Delta H$ crystallization, $\Delta H$ fusion	1992 (177)
sucrose	determination of crystallinity	$\Delta H$ crystallization, gravimetry	1993 (178)
glucose/fructose solutions	thermal behavior, investigation on glass transition temperature	$T_g$ , phase diagram, viscosity	1993 (179)
trehalose solution and other sugar solutions	thermal behavior of sugar solutions and nucleation phenomena study	$H_{\text{fusion}}$ nonequilibrium	1998 (180)
honey	determination of glass transition temperature/water content relationship thermal behavior	$H_{\text{crystallization}}$ nonequilibrium $T_g$ and water content	1999 (181)
oil	induction period oxidation analysis	$T_g$ , $\Delta H_{\text{exo}}$ , $\Delta H_{\text{endo}}$ , viscosity, % water, density, refraction index	1999 (182)
vitamin A and esters	stability	$T^{\circ}_{\text{onset}}$	2000 (183)
dehydrated apple	development of a method to determine water state in apple	measure of $T^{\circ}$ formation of kitol esters $\Delta H$ degradation RMN: measure of $T_1$ , spin-network relaxation time; and $T_2$ , spin-spin relaxation time DSC: $T_g$ , $\Delta H$ fusion frozen water, $T^{\circ}$ fusion	2000 (96)
meat	thermal behavior characterization	$T^{\circ}_{\text{onset}}$	1990 (185)
food carbohydrates	carbohydrate determination	$\Delta H$ , $C_p$	1998 (186)
milk-fat fractionation	measure of fat crystal properties	starch gelatinization phenomena	1997 (187)
cereal-based foods	crispness loss study		1996 (188)
biscuit dough	effect of major ingredients on baking process	Young's modulus, $\tan \delta$ , % water, $T_g$ DSC: $T^{\circ}_{\text{max}}$ ; TGA: $T^{\circ}_{\text{onset}}$ , $T^{\circ}_{\text{max}}$ DMTA: $T^{\circ}_{\text{onset}}$ , $T^{\circ}_{\text{max}}$ , $\Delta h/h_0$	1998 (102) 2000 (189,190)

Concerning honeys, the reference works in this area are those of White, Winters, and Martin (69, 70) for both the initial method development ( $\delta^{13}\text{C}$  measurements on honeys) and the setting of the improved method (internal standard method: measure of  $\delta^{13}\text{C}$  on honey proteins). These analytical developments were followed by a study on the detection of adulteration of honey by continuous-flow isotope ratio mass spectrometry (71). The method consisted of passing the sample through a GC combustion system and elemental analyzer inlets to determine the  $\delta^{13}\text{C}$  value in honey. The author claimed 1.6% of high-fructose corn syrup adulteration could be detected.

## DSC

Sometimes, chemical analytical methods need to be complemented by experiments using new indicators derived from physical analysis such as thermal analysis. The most widely used technique in this area is differential scanning calorimetry (DSC), which originated from the pharmaceutical (72, 73) and polymer material industries (74–80). The application of temperature-programmed scans causes some structural modifications (phase transitions, glass transition, etc.) or decompositions. Thermal techniques such as DSC and others can monitor these transformations by measuring their consequences: thermal effects (variation of temperature or energy), variation of physical properties of food products (heat capacity, Young's modulus, conductivity, variation of the volume, etc.), gas production, variation of mass, etc... These phenomena allow the determination of the type of transformation occurring in the studied products and determine their thermodynamic and kinetic properties.

The common transformations observable by DSC are the denaturation of proteins and their thermal stabilities (81–83); fusion or crystallization of carbohydrates, phase transitions of polysaccharides; thermal properties of frozen foods; fusion or crystallization of lipids and interactions with other chemical compounds (84, 85); gelatinization of native starch or starch in foods (86–91); and thermal history.

From 1992 to 1999, five important reviews on the applications of thermal analysis were published. Several analytical areas are involved, such as instrumentation, thermodynamic measurements, reaction kinetics, inorganic compounds, organic and polymeric materials, biological, and medical and pharmaceutical studies. (92, 93). Many aspects of the applications in the drug development process, such as calibration, purity determination, quantification of crystallinity, polymorphism, degradation, decomposition, and glass transition, have been thoroughly treated (72). In the area of food, DSC is also widely used, but its utilization is more recent than in other industrial domains. Foods are multicomponent systems containing proteins, carbohydrates, lipids, starch, and water. Therefore, multiple interactions can arise between food components and lead to some modifications of the thermal behavior of foods (72, 94). A good understanding of their thermal properties is essential for a good definition of product quality (95–103) and for detecting alteration (104) or adulteration (105–107). Moreover, a thermal analytical approach in food has great value in the quality assurance of food (108).

**Table 4** presents some additional calorimetric studies on foods with both the aims of each study and the parameter(s) measured to achieve the objective.

## IR, $^1\text{H}$ , AND $^2\text{H}$ NMR SPECTROSCOPIES

This review cannot be complete without taking into account the applications of spectroscopic techniques to food characterization and authentication.

**IR Spectroscopy.** One of the spectroscopic techniques most commonly used in the food product adulteration area or quality control of manufactured products is infrared spectroscopy (IR and mid-IR). The wavelength range is classically  $<2500\text{ cm}^{-1}$ .

A major advantage of IR spectroscopy versus other previously used techniques lies in its nondestructive nature, like NMR applications, which will be described later in this review.

From a general point of view, spectroscopic techniques yield structural information that constitutes a molecular fingerprint

**Table 5.** Main Work Using Spectroscopic Techniques (IR, Mid-IR, and NMR) on Foods for 7 Years (1994–2001)

analyzed products	aim of study	year (ref)
vegetable oils raspberry, currants (purée)	adulteration	1994 (197)
		1995 (192)
		1996 (193)
orange juices coffee		1995 (194)
		1996 (195)
hamburger virgin olive oils orange juices	characterization	1997 (196)
		2000 (197)
		2001 (198)
coffee coffee (robusta, arabica)		1996 (199)
		1996 (200)
chicken meats	cooking time-dependent spectral changes	1995 (201) 2000 (202)

of the sample. It makes sense to think that kind of technique could be used either as a characterization tool or as a technical means to detect food adulteration. Downey et al. (109) suggest various possible approaches using IR spectroscopy coupled with chemometric tools to perform food authentication.

**Table 5** presents the most interesting work published in the past seven years using IR spectroscopy for food characterization and food authentication.

With respect to honey, only one IR contribution (110) was reported from 1990 to 2000, probably because of the chemical complexity of this matrix, which is essentially constituted by various sugars (mono-, di-, tri-, and oligosaccharides) but also contains numerous aromatic substances, proteins, water, microscopic figurative elements such as pollens, vegetable cells, etc. The authors proposed a regression model (obtained by PLS methods) allowing the determination of the major constituents of honey (moisture, fructose, glucose, sucrose, and maltose) based on the IR measurements and classical physicochemical determinations (official methods of AOAC).

**NMR Spectroscopy.** For a few years, nuclear magnetic resonance (NMR) techniques such as  $^1\text{H}$  NMR,  $^2\text{H}$  NMR mono- or bidimensional (2D-NMR), and SNIF-NMR complemented the analysis possibilities offered by IR spectroscopy. The late 1980s and the early 1990s were particularly productive in reviews reporting the use of NMR applied to food materials with the aim of food characterization as well as adulteration detection (111–118). Vogel et al. (119) propose, in a study on fruit juices, a new screening method using  $^1\text{H}$  NMR combined with chemometrics. Their approach consists of applying principal component analysis (PCA) to reduce the data dimensionality from  $^1\text{H}$  NMR spectra. Effectively, when the analyzed substance is not pure (constituted by different types of molecules) as with a mixture, the generated  $^1\text{H}$  NMR spectrum is too complex to be interpreted visually. By applying PCA to these spectra, it is possible to combine correlated variables (peaks in spectra) to form a new smaller group of independent variables, which are called principal components. These components are oriented and constructed in order to explain the maximum variance contained in the original data. Results obtained by this method show this approach is very pertinent and adapted to detect adulteration because it allows a good discrimination between nonadulterated samples and samples adulterated by various compounds (sucrose, inverted beet sugar 50%, sodium benzoate, etc.).

More recently, Sacchi et al. (120) presented the high-field  $^1\text{H}$  NMR (600 MHz) contribution in olive oil characterization and geographical origin determination. This study is oriented toward minor component analysis of olive oil such as sterols,

saturated and unsaturated aliphatic aldehydes, and various volatile compounds. Results obtained indicate that samples are correctly classified in 96% of cases and that the discrimination between classes is sufficient to obtain a good characterization of geographical origin of olive oils. In the past year, Spyros et al. (121) presented a new facile method using  $^{31}\text{P}$  NMR to characterize olive oils to determine their geographical origin. This method is based on the phosphorylation of the free hydroxyls of the mono- and diglycerides with a specific reagent and the integration of the appropriate peaks in the  $^{31}\text{P}$  NMR spectrum. The method was tested with certain model compounds bearing labile protons with the purpose of quantitative measurements of 1,2-diglycerides/1,3-diglycerides ratios of virgin olive oils from different geographical origins.

In a characterization study of *Citrus* honeys, Lindner et al. (122) measured the D/H ratio and  $\delta^{13}\text{C}$  values on honey sugars using SMRI.

**SNIF-NMR.** Site-specific natural isotope fractionation nuclear magnetic resonance is probably the best answer to the question of adulterations. Stemming from the work of G. J. Martin and colleagues at l'Université de Nantes, France, SNIF-NMR is the most sophisticated and most specific method available for the determination of food product authenticity. Introduced in the early 1980s (123), this method is based on the measurement of deuterium/hydrogen (D/H) ratios at specific sites in a molecule. For example, to detect clandestine addition of sugar or modified sugar syrups in a juice or concentrate, the sample is fermented under controlled conditions and the resulting alcohol is distilled off. Alcohol recovery is monitored by determining the alcoholic grade of both the fermented juice and the distillate. D/H ratios are measured at the methyl (D/H)<sub>I</sub> and methylene (D/H)<sub>II</sub> sites of the ethanol molecule. The sample is declared to be adulterated if the (D/H)<sub>I</sub> value in ethanol derived from the sample falls below a certain level. It has been shown that the (D/H)<sub>I</sub> value is significantly lower in ethanol derived from beet sugar than in ethanol originating from grape or citrus fruits. One of the first applications of SNIF-NMR was to detect the adulteration of wines (124). Since then, numerous contributions of SNIF-NMR have been reported. Day et al. (125) showed the value of SNIF-NMR measurements coupled with AAS trace element analysis in the determination of the geographical origin of wines. Eleven trace elements were analyzed (K, Ca, Mg, Mn, Fe, Zn, Cu, Rb, Al, Sr, and Ba) by AAS, and five isotopic parameters [(D/H)<sub>W</sub><sup>Q</sup>;  $\delta^{18}\text{O}_{\text{W}}^{\text{Q}}$ ; (D/H)<sub>I</sub>; (D/H)<sub>II</sub>;  $\delta^{13}\text{C}_{\text{A}}^{\text{Q}}$ ], including two site-specific ratios, were determined using SNIF-NMR and IRMS. Martin et al. (126) applied SNIF-NMR alone or SNIF-NMR and stable isotope ratio analysis mass spectrometry (SIRA-MS) (127) to detect added sugar and to assess authentication of fruit juices. The influence of the deuterium content of the fermentation water on the isotopic parameters was shown, and a way for normalizing the results was proposed (adulteration triangle, interpretation rules for SNIF-NMR and SIRA-MS analysis applied to detection of beet sugar and/or cane sugar in fruit juice). The strength of this technique comes from its capacity to be applied to any raw material or any food product (128, 129). The only weakness of this method is the need for a large knowledge base or database for comparison purposes, but this limitation is diminishing as the SNIF-NMR method is more and more frequently used for food characterization or adulteration detection.

## CONCLUSION

With the objective of characterization of the food product, whether one adopts a global approach or a chemical compound approach, all of the techniques presented here are well suited

Table 6. Reviews and Overviews in Foods [Source: *Analytical Abstracts* (RSC)]

Abstracts Number	Technique(s) used (matrices studied)	Year	Abstracts Number	Technique(s) used (matrices studied)	Year
12H269	General	1998	6H243	HPLC-MS	1998
9H245	General	1998	3H238	HPLC(for peptides analysis)	1998
3H233	General	1998	2H173	HPLC	1999
4H219	Developments in food	1999	11H266	HPLC + GC	1999
1H222	Authentication	1999	6H200	HPLC + GC-MS	1999
8E4	Purity control measuring techniques	1999	9H244	HPIC	1999
8H262	General	2000	11H259	HPLC-Chemiluminescence	1999
10H228	General (L-ascorbic acid in plants)	2000	12H263	HPLC+ELISA+RIA	2000
12H266	General (Dtmn of SO <sub>2</sub> )	2000	11H224	HPLC	2000
10H218	General (chromatography of tocopherols and tocotrienols)	2000	9H301	HPIC	2000
10H230	General (dtmn of tocopherols)	2000	1H341	HPLC (aflatoxin B1)	2000
3H422	General (Quality control of food by enzymatic analysis)	2000	10H206	HPLC + GC-MS (bioactive alkaloids)	2000
8F63	General (speciation of As in food)	2000	10H204	HPLC (carboxylic acids)	2000
4F25	General (speciation of trace elements by ICP-MS)	2000	11H236	HPLC (carotenoids, nutriments, retinoids, tocopherols)	2000
6H18	Spectrophotometry	1998	10H207		
6H241	HPIC	1998	10H229	HPLC (carotenoids)	2000
1H204	HPLC	1998	6H403	HPLC+GC+TLC (cholesterol oxidation products)	2000
11H293	HPLC	1998	10H234	HPLC (ellagitamins)	2000
4H15	HPLC	1998	8H266	HPLC (flavonoids)	2000
4H204	HPIC	1998	1H331	HPLC + GC-MS (food additives)	2000

and provide interesting information. The ideal is to, as much as possible, arrange several techniques to gather a set of additional data allowing a better characterization of the food from the physicochemical point of view. In such a context and in an approach by chemical compounds, it seems evident that chromatographic techniques such as HPLC and GC (and their coupled variants) are particularly well adapted to the characterization of the food from a molecular point of view without there being a real necessity of identifying the totality of detected compounds (chemometric treatment of the chromatograms). However, it is also evident that the characterization of products may not be attainable with a purely molecular or macromolecular vision and that the mineral constituent often turns out to be interesting and even necessary for the characterization. In this area, only spectroscopic techniques such as atomic absorption (AAS, AES, ICP-AES, etc.) can bring the expected answer. As for UV-visible spectrophotometry, it joins a molecular approach of the characterization but with the necessity

of knowing the colorimetric properties of the measured compounds. If the global approach of the characterization is chosen, the best results will be obtained from techniques stemming from the domain of the thermal analysis such as DSC. More and more, IR spectroscopy and NMR spectroscopy are used in association with chemometric treatment to characterize mixtures of chemical compounds and foods. Finally, IRMS turns out to be successful both for a global characterization of the sample and for a compound by compound characterization (GC-IRMS and GC-C-IRMS), too. For the purpose of detection of adulteration, two approaches are also possible: the global analysis and the search for tracer(s) of adulteration. In the first case, IRMS and the spectroscopic techniques will doubtless give the best results, whereas in the second case a better approach will be to use chromatographic techniques, optical microscopy, and GC-IRMS. Besides, the significant development of data processing software (Statistica, S-Plus, Statgraphics, Unscrambler, etc.) provides considerable help in the resolution of the problems of charac-



Table 7. Reviews and Overviews in Foods [Source: *Analytical Abstracts* (RSC)]

Abstracts Number	Technique(s) used (matrices studied)	Year	Abstracts Number	Technique(s) used (matrices studied)	Year
10H233	HPLC + HPLC-electrospray (phytosterols)	2000	3C115	Online-NIR	1998
10F181	HPLC (thiamine)	2000	1A28	IR	1999
10H200	HPLC + TLC + CE (tetracycline antibiotics)	2000	4H222	NIR	1999
6H240	GC-MS	1998	7H237	IR	1999
10H265	GC	1998	1H330	NMR	2000
9H240	GC-MS + Sensors	1999			
11H266	GC-MS + HPLC	1999			
6H200	GC-MS + HPLC	1999			
11H222	GC-SPME	2000			
10H206	GC-MS + HPLC-MS	2000			
6H403	GC + HPLC + TLC	2000			
1H331	GC-MS + HPLC	2000			
10H248	GC-MS (phenylurea+other pesticides)	2000			
10H299	GC (unsaponifiable organic compounds in fat containing foods)	2000			
8H270	GC + GC-MS (volatiles aroma compounds)	2000			
9F20 12H209	AAS	1999			
6H183	Multiresidue methods	1999			
8F18	AAS	2000			
7H232	Py-IRMS	1999			

terization as well as in the search for and the detection of nonconformities and adulterations. Supplementing the classical chemometric tools, such as PCA, LDA, HCA, SIMCA and PLS methods, we see interesting developments of various solutions based on artificial neural networks applied to food problems. The main advantages of these “neuromimetic” structures are their robustness faced with fuzzy data and their capacity to resolve problems containing nonlinear solutions. The future of the analysis of foodstuffs seems to be linked to the increasing development of the analytical solutions marrying powerful analytical devices and data processing software such as the headspace GC-MS coupling, known as “Chemensor” (from Agilent Technology) or “Prometheus” (from Alpha MOS), which is a headspace MS system.

#### ABBREVIATIONS USED

PCA, principal component analysis; LDA, linear discriminant analysis; HCA, hierarchical cluster analysis; SIMCA, soft

independent modeling of class analogy; PLS, partial least squares; CVA, canonical variate analysis; ANN, artificial neural network; HPLC, high-performance liquid chromatography; GC, gas chromatography; MS, mass spectrometry; GC-FTIR, GC–Fourier transform infrared spectroscopy; AAS, atomic absorption spectroscopy; AES, atomic emission spectroscopy; ICP, inductively coupled plasma; IRMS, isotopic ratio mass spectrometry; TGA, thermogravimetric analysis; DSC, differential scanning calorimetry; IR, infrared spectroscopy; NMR, nuclear magnetic resonance spectroscopy; SNIF-NMR, site-specific natural fractionation nuclear magnetic resonance spectroscopy; HPIC-PAD, high-performance ionic chromatography–pulsed amperometric detection.

#### ACKNOWLEDGMENT

We thank Dr. Tom Forrest for reviewing the manuscript and Pr. Daniel Cabrol-Bass for helpful discussions about chemometric approaches.

## LITERATURE CITED

- (1) Dennis, M. J. Recent Developments in Food Authentication. *Analyst* **1998**, *123*, 151R–156R.
- (2) Activity reports of DGCCRF; 1997–1999; www.finances.gouv.fr/DGCCRF/activities/index-d.htm (2001).
- (3) Briandet, R.; Kemsley, E. K.; Wilson, R. H. Approaches to Adulteration Detection in Instant Coffees using Infrared Spectroscopy and Chemometrics. *J. Sci. Food Agric.* **1996**, *71*, 359–366.
- (4) Maurizio, A. Beiträge zur Quantitativen Pollenanalyse des Honigs. 3. Absoluter Gehalt Pflanzlicher Bestandteile in Esparsette, Luzerne, Orangen und Rasphonigen. *Ann. Abeille* **1958**, *11*, 93–106.
- (5) Maurizio, A.; Louveaux, J. *Pollens des plantes Mellifères d'Europe*; Union des Groupements Apicoles Français, 1965.
- (6) Louveaux, J. Pollenanalyse Einiger Kanadischer Honig. *Z. Bienenforsch.* **1966**, 195–202.
- (7) Louveaux, J.; Maurizio, A.; Vorwohl, G. Methods of Melissopolynology. *Bee World* **1978**, *59* (4), 139–157.
- (8) Cortopassi-Laurino, M.; Gelli, D. S. Analyse Pollinique, Propriétés Physico-chimiques et Action Antibactérienne des Miels d'Abeilles Africanisées *Apis mellifera* et de Méliponisées du Brésil. *Apidologie* **1991**, *22*, 61–73.
- (9) Thrasyvoulou, A.; Manikis, J. Some Physicochemical and Microscopic Characteristics of Greek Unifloral Honey. *Apidologie* **1995**, *26*, 441–452.
- (10) Kerkvliet, J. D.; Shrestha, M.; Tuladhar, K.; Manandhar, H. Microscopic Detection of Adulteration of Honey with Cane Sugar and Cane Sugar Products. *Apidologie* **1995**, *26*, 131–139.
- (11) Kerkvliet, J. D.; Meijer, H. A. J. Adulteration of honey: relation between microscopic analysis and  $\delta^{13}\text{C}$  measurements. *Apidologie* **2000**, *31*, 717–726.
- (12) Anklam, E. A review of the analytical methods to determine the geographical and botanical origin of honey. *Food Chem.* **1998**, *63* (4), 549–562.
- (13) Dustmann, J. H.; Bote, K. Raster-electronenmikroskopische Studien an Pollen aus Bienenhonig. I. Vergleich verschiedener Präparationsmethoden. *Apidologie* **1985**, *16* (3), 331–340.
- (14) Dustmann, J. H.; Bote, K. Raster-electronenmikroskopische Studien an Pollen aus Bienenhonig. II. Vergleich der Exine-Strukturen trockener und in Honig expandierter Pollen bei verschiedenen Apfel- bzw. Zierapfelsorten. *Gartenbauwissenschaft* **1987**, *52*, 271–278.
- (15) Dustmann, J. H.; Ohe, K. V. D. Scanning Electron Microscopic Studies on Pollen from Honey. IV. Surface Pattern of Pollen of *Sapium sebiferum* and *Euphorbia* spp. (Euphorbiaceae). *Apidologie* **1993**, *24*, 59–66.
- (16) Ohe, K. V. D. Scanning Electron Microscopic Studies of Pollen from Apple Varieties. 6th Pollination Symposium. *Acta Hort.* **1991**, 405–409.
- (17) Erdtman, G. The Acetolysis Method. *Svensk Bot. Tidsskr.* **1960**, *54* (4), 561–564.
- (18) Blanch, G. P.; Mar Caja, M.; Ruiz del Castillo, M. L.; Herraiz, M. Comparison of Different Methods for the Evaluation of the Authenticity of Olive Oil and Hazelnut Oil. *J. Agric. Food Chem.* **1998**, *46*, 3153–3157.
- (19) Ruiz del Castillo, M. L.; Mar Caja, M.; Herraiz, M.; Blanch, G. P. Rapid Recognition of Olive Oil Adulterated with Hazelnut Oil by Direct Analysis of the Enantiomeric Composition of Filiberstone. *J. Agric. Food Chem.* **1998**, *46*, 5128–5131.
- (20) Silva, B. M.; Andrade, P. B.; Mendes, G. C.; Valentao, P.; Seabra, R. M.; Ferreira, M. A. Analysis of Phenolic Compounds in the Evaluation of Commercial Quince Jam Authenticity. *J. Agric. Food Chem.* **2000**, *48*, 2853–2857.
- (21) Mouly, P.; Gaydou, E. M.; Auffray, A. Simultaneous separation of flavone glycosides and polymethoxylated flavones in citrus juices using liquid chromatography. *J. Chromatogr. A* **1998**, *800*, 171–179.
- (22) Guyot, S.; Marnet, N.; Laraba, D.; Sanoner, P.; Drilleau, J. F. Reversed-Phase HPLC following Thiolytic for Quantitative Estimation and Characterization of the Four Classes of Phenolic Compounds in Different Tissue Zones of a French Cider Apple Variety (*Malus domestica* Var. Kermerrien). *J. Agric. Food Chem.* **1998**, *46*, 1698–1705.
- (23) Bengoechea, L. M.; Sancho, A. I.; Bartolomé, B.; Estrella, I.; Gomez-Cordovés, C.; Hernandez, M. T. Phenolic Composition of Industrially Manufactured Purées and Concentrates from Peach and Apple Fruits. *J. Agric. Food Chem.* **1997**, *45*, 4071–4075.
- (24) Mohler-Smith, A.; Nakai, S. Classification of Cheese Varieties by Multivariate Analysis of HPLC Profiles. *Can. Inst. Food Sci. Technol. J.* **1990**, *23* (1), 53–58.
- (25) Kawaii, S.; Tomono, Y.; Katase, E.; Ogawa, K.; Yano, M. HL-60 Differentiating Activity and Flavonoid Content of the readily Extractable Fraction Prepared from Citrus Juices. *J. Agric. Food Chem.* **1999**, *47*, 128–135.
- (26) Robards, K.; Li, X.; Antolovich, M.; Boyd, S. Characterization of Citrus by Chromatographic Analysis of Flavonoids. *J. Sci. Food Agric.* **1997**, *75*, 87–101.
- (27) Blanco, D.; Quintanilla, M. E.; Mangas, J. J.; Gutierrez, M. D. Determination of Organic Acids in Apple Juice by Capillary Liquid Chromatography. *J. Liq. Chromatogr. Relat. Technol.* **1996**, *19* (16), 2615–2621.
- (28) McDowell, I.; Taylor, S.; Gay, C. The Phenolic Pigment Composition of Black Tea Liquors—Part I: Predicting Quality. *J. Agric. Food Chem.* **1995**, *69*, 467–474.
- (29) McDowell, I.; Taylor, S.; Gay, C. The Phenolic Pigment Composition of Black Tea Liquors—Part II: Discriminating origin. *J. Agric. Food Chem.* **1995**, *69*, 475–480.
- (30) Calabrese, M.; Stancher, B.; Riccobon, P. High-Performance Liquid Chromatography Determination of Proline Isomers in Italian Wines. *J. Agric. Food Chem.* **1995**, *69*, 361–366.
- (31) Garcia-Parrilla, M. C.; Gonzalez, G. A.; Heredia, F. J.; Troncoso, A. M. Differentiation of Wine Vinegars Based on Phenolic Composition. *J. Agric. Food Chem.* **1997**, *45*, 3487–3492.
- (32) Moreno-Arribas, V.; Pueyo, E.; Polo, M. C.; Martin-Alvarez, P. J. Changes in the Amino Acid Composition of the Different Nitrogenous Fractions during the Aging of Wine with Yeast. *J. Agric. Food Chem.* **1998**, *46*, 4042–4051.
- (33) Garcia-Viguera, C.; Zafrilla, P.; Tomas-Barberan, F. A. Determination of Authenticity of Fruit Jams by HPLC Analysis of Anthocyanins. *J. Sci. Food Agric.* **1997**, *73*, 207–213.
- (34) Kellner, R.; Mermet, J.-M.; Otto, M.; Widmer, H. M. *Hyphenated Techniques*; Wiley-VCH Verlag: Weinheim, Germany, 1998; Vol. 14, pp 827–855.
- (35) Sivertsen, H. K.; Holen, B.; Nicolaysen, F.; Risvik, E. Classification of French Red Wines According to Their Geographical Origin by the Use of Multivariate Analyses. *J. Sci. Food Agric.* **1999**, *79*, 107–115.
- (36) Nogueira, J. M. F.; Nascimento, A. M. D. Analytical Characterisation of Madeira Wine. *J. Agric. Food Chem.* **1999**, *47*, 566–575.
- (37) König, T.; Schreier, P. Application of Multivariate Statistical Methods to Extend the Authenticity Control of Flavour Constituents of Apple Juice. *Z. Lebensm. Unters. Forsch. A* **1999**, *208*, 130–133.
- (38) Angerosa, F.; Di Giacinto, L.; Vito, R.; Cumitini, S. Sensory Evaluation of Virgin Olive Oils by Artificial Neural Network Processing of Dynamic Headspace Gas Chromatographic Data. *J. Sci. Food Agric.* **1996**, *72*, 323–328.
- (39) Soedjak, H. S. Colorimetric Micromethod for Protein Determination with Erythrosin B. *Anal. Biochem.* **1994**, *220*, 142–148.
- (40) Bradford, M. A Rapid Sensitive Method for the Quantitation of Microgram Quantities Utilizing the Principle of Protein-Dye Binding. *Anal. Biochem.* **1976**, *72*, 248–254.
- (41) Bio-Rad Protein Assay. Life Science Research, Bio-Rad, 3 boulevard Raymond Poincaré, F-92430 Marnes-La-Coquette, France, 2000.

- (42) Wilkinson, M. G.; Guinee, T. D.; O'Callaghan, D. M.; Fox, P. F. Effect of Commercial Enzymes on Proteolysis and Ripening in Cheddar Cheese. *Lait* **1992**, 449–459.
- (43) Johnson, A. W.; McCaldin, D. J. The Reaction of Ninhydrin with Cyclic  $\alpha$ -Imino-acids. *J. Chem. Soc.* **1958**, 817–822.
- (44) Wallace, J. M.; Fox, P. F. Rapid Spectrophotometric and Fluorimetric methods for Monitoring Nitrogenous (proteinaceous) Compounds in Cheese and Cheese Fractions: a review. *Food Chem.* **1998**, 62 (2), 217–224.
- (45) Chen, W.; Pan, Z. X.; Li, L.; Song, Z. T.; Zhang, M. S. Determination of Trace Selenium in Foodstuffs using Rank Annihilation Factor Analysis-fluorimetry. *Fenxi Huaxue* **1994**, 22 (10), 1054–1056.
- (46) Zhu, Q. Z.; Yang, H. H.; Li, D. H.; Xu, J. G. Determination of Nucleic Acids using Phosphine 3R as a Fluorescence Probe. *Anal. Chim. Acta* **1999**, 394 (2–3), 177–184.
- (47) Yang, H. H.; Zhu, Q. Z.; Chen, Q. Y.; Li, D. H.; Xu, J. G. Application of Magdala Red as a Fluorescence Probe in the Determination of Nucleic Acids. *Fresenius' J. Anal. Chem.* **2000**, 366 (3), 303–306.
- (48) White, J. W.; Rujdyj, J. R. Proline Content of United States Honeys. *J. Apic. Res.* **1978**, 17 (2), 89–93.
- (49) Davies, A. M. C.; Harris, R. G. Free Amino Acid Analysis of Honeys from England and Wales: Application to the Determination of the Geographical Origin of Honeys. *J. Apic. Res.* **1982**, 21 (3), 168–173.
- (50) Fernandez-Muino, M. A.; Sancho, M. T. Direct Enzymatic Analysis of Glycerol in Honey: a Simplified Method. *J. Sci. Food Agric.* **1996**, 71, 141–144.
- (51) Mato, I.; Huidobro, J. F.; Sanchez, M. P.; Muniategui, S.; Fernandez-Muino, M. A.; Sancho, M. T. Enzymatic Determination of Total D-Gluconic Acid in Honey. *J. Agric. Food Chem.* **1997**, 45, 3550–3553.
- (52) Val, A.; Huidobro, J. F.; Sanchez, M. P.; Muniategui, S.; Fernandez-Muino, M. A.; Sancho, M. T. Enzymatic Determination of Galactose and Lactose in Honey. *J. Agric. Food Chem.* **1998**, 46, 1381–1385.
- (53) Mato, I.; Huidobro, J. F.; Sanchez, M. P.; Muniategui, S.; Fernandez-Muino, M. A.; Sancho, M. T. Enzymatic Determination of L-Malic Acid in Honey. *Food Chem.* **1998**, 62 (4), 503–508.
- (54) McLellan, A. R. Calcium, Magnesium, Potassium, Sodium in Honey and in Nectar Secretion. *J. Apic. Res.* **1975**, 14 (2), 57–61.
- (55) Petrovic, Z. T.; Mandic, M.; Grgic, J.; Grgic, Z.; Besic, J. Selenium Levels in some Species of Honey in Eastern Croatia. *Dtsch. Lebensm.-Rundsch.* **1993**, 89, 46–48.
- (56) Julshamn, K.; Maage, A.; Wallin, H. C. Determination of Magnesium and Calcium in Foods by Atomic Absorption Spectrometry after Microwave Digestion: NMKL Collaborative Study. *J. Assoc. Off. Anal. Chem.* **1998**, 81 (6), 1202–1208.
- (57) Baxter, M. J.; Crews, H. M.; Dennis, M. J.; Goodall, I.; Anderson, D. The Determination of the Authenticity of Wine from Its Trace Element Composition. *Food Chem.* **1997**, 60 (3), 443–450.
- (58) Fresno, J. M.; Prieto, B.; Urdiales, R.; Sarmiento, R. M. Mineral Content of Some Spanish Cheese Varieties. Differentiation by Source of milk and by Variety from their Content of main and Trace Elements. *J. Sci. Food Agric.* **1995**, 69, 339–345.
- (59) Leblebici, J.; Volkan, M. Sample Preparation for Arsenic, Copper, Iron and Lead. Determination in Sugar. *J. Agric. Food Chem.* **1998**, 46, 173–177.
- (60) Prats-Moya, S.; Grané-Teruel, N.; Berenguer-Navarro, V.; Martin-Carratala, M. L. Inductively Coupled Plasma Application for the Classification of 19 Almond Cultivars Using Inorganic Element Composition. *J. Agric. Food Chem.* **1997**, 45, 2093–2097.
- (61) Rodriguez-Otero, J. L.; Paseiro, P.; Simal, J.; Cepeda, A. Mineral Content of the Honeys Produced in Galicia (North-west Spain). *Food Chem.* **1994**, 49, 169–171.
- (62) Vinas, P.; Lopez-Garcia, I.; Lanzon, M.; Hernandez-Cordoba, M. Direct Determination of Lead, Cadmium, Zinc; Copper in Honey by Electrothermal Atomic Absorption Spectrometry using Hydrogen Peroxide as a Matrix Modifier. *J. Agric. Food Chem.* **1997**, 45, 3952–3956.
- (63) Moussa, I. Vérification de l'Authenticité des Miels Monofloraux par Analyse Élémentaires et Isotopique; Laboratoire de la Répression des Fraudes, Parc Euromédecine, 205 rue de la Croix Verte, 34196 Montpellier cedex 5, France, 1992.
- (64) Lapierre, L. Contrôle de l'Authenticité des Jus d'Agrumes et des Miels par Analyse Isotopique et Élémentaire. Thèse soutenue à l'Université des Sciences de Montpellier, 1996.
- (65) Simpkins, W. A.; Louie, H.; Wu, M.; Harrison, M.; Goldberg, D. Trace elements in Australian orange juice and other products. *Food Chem.* **2000**, 71, 423–433.
- (66) Sun, L. X.; Danzer, K.; Thiel, G. Classification of Wine Samples by Means of Artificial Neural Networks and Discrimination Analytical Methods. *Fresenius' J. Anal. Chem.* **1997**, 359, 143–149.
- (67) White, J. W. Internal Standard Stable Carbon Isotope Ratio Method for Determination of C-4 plants Sugars in Honey: Collaborative Study; Evaluation of Improved Protein Preparation Procedure. *J. Assoc. Off. Anal. Chem.* **1992**, 75 (3), 543–548.
- (68) Meier-Augenstein, W. Applied gas chromatography coupled-to-isotope ratio mass spectrometry. *J. Chromatogr. A* **1999**, 842, 351–371.
- (69) White, J. W.; Winters, K. Honey protein as internal standard for stable carbon isotope ratio detection of adulteration of honey. *J. Assoc. Off. Anal. Chem.* **1989**, 72 (6), 907–911.
- (70) White, J. W.; Winters, K.; Martin, P.; Rossmann, A. Stable Carbon Isotope Ratio Analysis of Honey: Validation of Internal Standard Procedure for Worldwide Application. *J. Assoc. Off. Anal. Chem.* **1998**, 81 (3), 610–619.
- (71) Hernandez, H. Detection of adulteration of honey: application of continuous-flow IRMS. *VAM Bull.* **1998**, 18 (Spring), 12–14.
- (72) Clas, S.-D.; Dalton, C. R.; Hancock, B. C. Differential scanning calorimetry: applications in drug development. *PSTT* **1999**, 2 (8), 311–320.
- (73) Poirier, L. J. Characterization of pharmaceuticals by thermal analysis. *Int. Lab.* **1991**, 21, 1, 26, 28–30, 32.
- (74) Clas, S.-D. *Thermochim. Acta* **1996**, 288, 83–96.
- (75) Gehenot, A.; Rao, R. C.; Maire, G. *Int. J. Pharm.* **1988**, 45, 13–17.
- (76) Morgan, D. R.; Kalanchandra, S.; Shobha, H. K.; Gunduz, N.; Stejskal, E. O. Analysis of a Dimethacrylate Copolymer (Bis-GMA and TEGDMA) Network by DSC and  $^{13}\text{C}$  solution and Solid-State NMR spectroscopy. *Biomaterials* **2000**, 21, 1897–1903.
- (77) Pires, J.; Brotas De Carvalho, M.; Carvalho, A. P.; Guil, J. M. Perdigon-Melon Heat of Adsorption of N-Hexane by Thermal Gravimetry with Differential Scanning Calorimetry (TG-DSC): A Tool for Textural Characterization of Pillared Clays. *Clays Clay Miner.* **2000**, 48 (3), 385–391.
- (78) Sbirrazzuoli, N.; Girault, Y.; Elégant, L. Kinetic investigation of the polymerization of an epoxy resin by DSC and temperature profile determination during cure. *Angew. Makromol. Chem.* **1993**, 211, 195–204.
- (79) Vyazovkin, S.; Sbirrazzuoli, N. Effect of viscosity on the kinetics of initial cure stages. *Macromol. Chem. Phys.* **2000**, 201, 199–203.
- (80) Yamamoto, K.; Momota, M.; Katayama, S.; Narita, K. Determination of the Purity of Multicomponent Organic Substances by DSC. *Anal. Sci.* **1998**, 14 (3), 599–602.
- (81) Gringberg, V. Y.; Burova, T. V.; Haertlé, T.; Tolstoguzov, V. B. Interpretation of DSC on Protein Denaturation Complicated by Kinetic and Irreversible Effects. *J. Biotechnol.* **2000**, 79, 269–280.

- (82) Kulmyrzaev, A.; Bryant, C.; McClements, D. J. Influence of Sucrose on the Thermal Denaturation, Gelation and Emulsion Stabilisation of Whey Proteins. *J. Agric. Food Chem.* **2000**, *48*, 1593–1597.
- (83) Relkin, P. Differential Scanning Calorimetry: a useful tool for studying protein denaturation. *Thermochim. Acta* **1994**, *246*, 371–386.
- (84) Chevallier, S.; Colonna, P. Thermal Analysis of Protein-Starch Interactions at Low Moisture Contents. *Sci. Aliments* **1999**, *19*, 167–182.
- (85) Villwock, V. K.; Eliasson, A. C.; Silverio, J.; BeMiller, J. N. Starch-Lipid Interactions in Common, Waxy, ae du, and ae su2 Maize Starches Examined by Differential Scanning Calorimetry. *Cereal Chem.* **1999**, *76* (2), 292–298.
- (86) Barreto, P. L.; Beirao, L. H.; Soldi, M. S.; Soldi, V. Studies on Differential Scanning Calorimetry and Thermogravimetry of Tilapia (*Oreochromis nilotica*) Surimi, Surimi/Starch and Surimi/Starch/Carrageenan Systems. *J. Food Sci. Technol.* **2000**, *37* (3), 265–271.
- (87) Chiotelli, E.; Rolée, A.; Le Meste, M. Effect of Sucrose on the Thermomechanical Behaviour of Concentrated Wheat and Waxy Corn Starch-Water Preparations. *J. Agric. Food Chem.* **2000**, *48*, 1327–1339.
- (88) Morikawa, K.; Nishinari, K. Effects of Concentration Dependence of Retrogradation Behaviour of Dispersions for Native and Chemically Modified Potato Starch. *Food Hydrocolloids* **2000**, *14*, 395–401.
- (89) Morikawa, K.; Nishinari, K. Rheological and DSC Studies of Gelatinization of Chemically Modified Starch Heated at Various Temperatures. *Carbohydr. Polym.* **2000**, *43*, 241–247.
- (90) Takahashi, K.; Kondo, H.; Kuroiwa, H.; Yokote, Y.; Hattori, M. Reversible Thermal Transition of Soluble Branched Chains from Slightly Acid-treated Potato Starch. *Biosci., Biotechnol., Biochem.* **2000**, *64* (7), 1365–1372.
- (91) Wang, Y. J.; Wang, L. Structures and Properties of Commercial Maltodextrins from Corn, Potato and Rice Starches. *Starch/Staerke* **2000**, *52*, 296–304.
- (92) Dollimore, D. Thermal Analysis. *Anal. Chem.* **1992**, *64*, 147R–153R.
- (93) Dollimore, D.; Lerdkanchanaporn, S. Thermal Analysis. *Anal. Chem.* **1998**, *70* (12), 27R–35R.
- (94) John, A.; Shastri, P. N. Studies on Food Macromolecules by Differential Scanning Calorimetry: A Critical Appraisal. *J. Food Sci. Technol.* **1998**, *35* (1), 1–14.
- (95) Aguilera, J. M.; Gloria, H. Determination of Oil in Fried Potato Products by Differential Scanning Calorimetry. *J. Agric. Food Chem.* **1997**, *45*, 781–785.
- (96) Cornillon, P. Characterization of Osmotic Dehydrated Apple by NMR and DSC. *Lebensm. Wiss. -Technol.* **2000**, *33*, 261–267.
- (97) Curini, R.; D'Ascenzo, G.; Materazzi, S.; Chiacchierini, E.; Angelis Curtis, S.; Lucchetti, M. C. Characterization of Coffees by Thermoanalytical Methods. *Ann. Chim.* **1991**, *81* (11–12), 625–638.
- (98) Gloria, H.; Aguilera, J. M. Assessment of the Quality Oils by Differential Scanning Calorimetry. *J. Agric. Food Chem.* **1998**, *46*, 1363–1368.
- (99) Goff, H. D. The use of thermal analysis in the development of a better understanding of frozen food stability. *Pure Appl. Chem.* **1995**, *67* (11), 1801–1808.
- (100) Kerr, W. L.; Reid, D. S. The Use of Stepwise Differential Scanning Calorimetry for Thermal Analysis of Foods. *Thermochim. Acta* **1994**, *246*, 299–308.
- (101) Niediek, E. A. Amorphous Sugar, Its Formation and Effect on Chocolate Quality. *Manuf. Confect.* **1991**, *6*, 91–95.
- (102) Roudaut, G.; Dacremont, C.; Le Meste, M. Is Tg responsible for the Crispness Loss of Cereal Based Foods During Storage? *Biopolym. Sci.* **1998**, *7* (28–30), 283–289.
- (103) Sbarato, L. Fast Analytical methods. *Ind. Aliment.* **1996**, *35* (344), 43–45.
- (104) Fiala, M.; Honikel, K. O. Application of differential calorimetry. 2. Detection of additives in meat. *Fleischforschung* **1995**, *75* (8), 1013–1018.
- (105) Coni, E.; Pasquale, P.; Coppolelli, P.; Bocca, A. Detection of Animal Fats in Butter by Differential Scanning Calorimetry: A Pilot Study. *J. Am. Oil. Chem.* **1994**, *71* (8), 807–810.
- (106) Cordella, C.; Antinelli, J. F.; Aurieres, C.; Faucon, J. P.; Cabrol-Bass, D.; Sbirrazzuoli, N. Use of Differential Scanning Calorimetry (DSC) as a New Technique for Detection of Adulteration in Honeys. 1. Study of Adulteration Effect on Honey Thermal Behavior. *J. Agric. Food Chem.* **2001**, *50*, 203–208.
- (107) Tunick, M. H. DSC Analysis of Dairy Products. In *Proceedings of the 26th Conference of the North American Thermal Analysis Society, Cleveland*; Wilkins: Baltimore, MD, 1998; Vol. 7, pp 13–15.
- (108) Farkas, J.; Mohacsi-Farkas, C. Application of Differential Scanning Calorimetry in Food Research and Food Quality Assurance. *J. Therm. Anal.* **1996**, *47*, 1787–1803.
- (109) Downey, G. Food and Food Ingredient Authentication by Mid-Infrared Spectroscopy and Chemometrics. *Trends Anal. Chem.* **1998**, *17* (7), 419–424.
- (110) Qui, P. Y.; Ding, H. B.; Tang, Y. K.; Xu, R. J. Determination of Chemical Composition of Commercial Honey by Near-Infrared Spectroscopy. *J. Agric. Food Chem.* **1999**, *47* (7), 2760–2765.
- (111) Ablett, S. Overview of NMR Applications in Food Science. *Trends Food Sci. Technol.* **1992**, *3* (8), 246–250.
- (112) Beauvallet, C.; Renou, J.-P. Applications of NMR spectroscopy in meat research. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 241–245.
- (113) Berendsen, H. J. C. Rationale For Using NMR to Study Water Relations in Foods and Biological Tissues. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 202–205.
- (114) Fischman, A. J.; Tompkins, R. G. Perspective on the applications of NMR in nutrition. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 220–225.
- (115) Gidley, M. J. High-resolution solid-state NMR of food materials. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 231–236.
- (116) Guillou, C.; Remaud, G.; Martin, G. J. Applications of NMR to the Characterization and Authentication of Foods and Beverages. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 197–201.
- (117) O'Brien, J. Authentication and Quality Assessment of Food Products. *Trends Food Sci. Technol.* **1992**, *3* (8/9), 19–22.
- (118) Widmer, W. W.; Cancelon, P. F.; Nagy, S. Methods for Determining the Adulteration of Citrus Juices. *Trends Food Sci. Technol.* **1992**, *3* (11), 278–286.
- (119) Vogels, J. T. W. E.; Terwel, L.; Tas, A. C.; Van der Berg, F.; Dukel, F.; Van der Greef, J. Detection of Adulteration in Orange Juices by a New Screening Method Using Proton NMR Spectroscopy in Combination with Pattern Recognition Techniques. *J. Agric. Food Chem.* **1996**, *44*, 175–180.
- (120) Sacchi, R.; Mannina, L.; Fiordiponti, P.; Barone, P.; Paolillo, L.; Patumi, M.; Segre, A. Characterization of Italian Extra Virgin Olive Oils Using <sup>1</sup>H NMR Spectroscopy. *J. Agric. Food Chem.* **1998**, *46*, 3947–3951.
- (121) Spyros, A.; Dais, P. Application of <sup>31</sup>P NMR Spectroscopy in Food Analysis. 1. Quantitative Determination of the Mono- and Diglyceride Composition of Olive Oils. *J. Agric. Food Chem.* **2000**, *48*, 802–805.
- (122) Lindner, P.; Bermann, E.; Gamernik, B. Characterization of Citrus Honey by Deuterium NMR. *J. Agric. Food Chem.* **1996**, *44*, 139–140.
- (123) Martin, G. J.; Martin, M. L. Deuterium labeling at the natural abundance level as studied by high field quantitative <sup>2</sup>H NMR. *Tetrahedron Lett.* **1981**, *22* (36), 3525–3528.
- (124) Martin, G. J.; Martin, M. L. *Mod. Methods Plant Anal. (Wine Anal.)* **1988**, *6*, 258–275.

- (125) Day, M. P.; Zhang, B.; Martin, G. J. Determination of the Geographical Origin of Wine Using Joint Analysis of Elemental and Isotopic Composition. II—Differentiation of the Principal Production Zones in France for the 1990 Vintage. *J. Sci. Food Agric.* **1995**, *67*, 113–123.
- (126) Martin, G. G.; Wood, R.; Martin, G. J. Detection of Added Beet Sugar in Concentrated and Single Strength Fruit Juices by Deuterium Nuclear Magnetic Resonance (SNIF-NMR Method): Collaborative Study. *J. AOAC Int.* **1996**, *79* (4), 917–928.
- (127) Martin, G. G.; Hanote, V.; Lees, M.; Martin, Y. L. Interpretation of combined 2H SNIF/NMR and 13C SIRA/MS analyses of fruit juices to detect added sugar. *J. AOAC Int.* **1996**, *79* (1), 62–72.
- (128) Remaud, G.; Debon, A. A.; Martin, Y.-L.; Martin, G. G.; Martin, G. J. Authentication of Bitter Almond Oil and Cinnamon Oil: Application of the SNIF-NMR Method to Benzaldehyde. *J. Agric. Food Chem.* **1997**, *45*, 4042–4048.
- (129) Remaud, G.; Martin, Y.-L.; Martin, G. G.; Martin, G. J. Detection of Sophisticated Adulteration of Natural Vanilla Flavors and Extracts: Application of the SNIF-NMR Method to Vanillin and *p*-Hydroxybenzaldehyde. *J. Agric. Food Chem.* **1997**, *45*, 859–866.
- (130) Wootton, M.; Edwards, R. A.; Faraji-Haremi, R. Effect of Accelerated Storage Conditions on The Chemical Composition and Properties of Australian Honeys. 2. Changes in Sugar and Free Amino Acid Contents. *J. Apic. Res.* **1976**, *15* (1), 29–34.
- (131) Low, N. H.; Nelson, D. L.; Sporns, P. Carbohydrate Analysis of Western Canadian Honeys and their Nectar Sources to Determine the Origin of Honey Oligosaccharides. *J. Apic. Res.* **1988**, *27* (4), 245–251.
- (132) Davies, A. M. C. Amino Acid Analysis of Honeys From Eleven Countries. *J. Apic. Res.* **1975**, *14* (1), 29–39.
- (133) Davies, A. M. C. The Application of Amino Acid Analysis to the Determination of the Geographical Origin of Honey. *J. Food Technol.* **1976**, *11*, 515–523.
- (134) Perez, C.; Conchello, P.; Arino, A.; Yanguela, J.; Herrera, A. Dosage des Acides Aminés des Protéines de Différents Miels Espagnols. *Sci. Aliments* **1989**, *9*, 203–207.
- (135) Bogdanov, S. Determination of Pinocembrin in Honey Using HPLC. *J. Apic. Res.* **1989**, *28* (1), 55–57.
- (136) Swallow, K. W.; Low, N. H. Analysis and Quantitation of the Carbohydrates in Honey Using High-Performance liquid Chromatography. *J. Agric. Food Chem.* **1990**, *38*, 1828–1832.
- (137) Andrade, P. Analysis of Honey Phenolic Acids by HPLC, its Application to Honey Botanical Characterisation. *J. Liq. Chromatogr. Relat. Technol.* **1997**, *20* (14), 2281–2288.
- (138) Martos, I.; Ferreres, F.; Tomas-Barberan, F. A. Identification of Flavonoid Markers for the Botanical Origin of Eucalyptus Honey. *J. Agric. Food Chem.* **2000**, *48*, 1498–1502.
- (139) Brückner, H.; Langer, M.; Lüpke, M.; Westhauser, T.; Godel, H. Liquid Chromatographic Determination of Amino Acid Enantiomers by Derivatization with *o*-phthalaldehyde and Chiral Thiols. Applications with Reference to Food Science. *J. Chromatogr. A* **1995**, *697*, 229–245.
- (140) Pawlowska, M.; Armstrong, D. W. Evaluation of Enantiomeric Purity of Selected Amino Acids in Honey. *Chirality* **1994**, *6*, 270–276.
- (141) Bogdanov, S.; Vit, P.; Kilchenmann, V. Sugar Profile and Conductivity of Stingless Bee Honeys from Venezuela. *Apidologie* **1996**, *27*, 445–450.
- (142) Del Nozal, M. J. High Performance liquid Chromatographic Determination of Organic Acids in Honeys From Different Botanical Origin. *J. Liq. Chromatogr. Relat. Technol.* **1998**, *21* (20), 3197–3214.
- (143) Sporn, P.; Plhak, L.; Friedrich, J. Alberta Honey Composition. *Food Res. Int.* **1992**, *25*, 93–100.
- (144) Cherchi, A.; Spanedda, L.; Tuberoso, C.; Cabras, P. Solid-Phase Extraction and High-Performance Liquid Chromatographic Determination of Organic Acids in Honey. *J. Chromatogr. A* **1994**, *669*, 59–64.
- (145) Lo Coco, F.; Valentini, C.; Novelli, V.; Ceccon, L. High-performance Liquid Chromatographic Determination of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde in Honey. *J. Chromatogr. A* **1996**, *749*, 95–102.
- (146) Ferreres, F.; Andrade, P.; Tomas-Barberan, F. A. Natural Occurrence of Abscisic Acid in Heather Honey and Floral Nectar. *J. Agric. Food Chem.* **1996**, *44*, 2053–2056.
- (147) Crews, C.; Startin, J. R.; Clarke, P. A. Determination of Pyrrolizidine Alkaloids in Honey from Selected Sites by Solid-Phase Extraction and HPLC-MS. *Food Addit. Contam.* **1997**, *14* (5), 419–428.
- (148) Martos, I.; Cossentini, M.; Ferreres, F.; Tomas-Barberan, F. A. Flavonoid Composition of Tunisian Honey and Propolis. *J. Agric. Food Chem.* **1997**, *45* (8), 2824–2829.
- (149) Ferreres, F.; Juan, T.; Pérez-Arquillué, C.; Herrera-Martache, A.; Garcia-Viguera, C.; Tomas-Barberan, F. A. Evaluation of Pollen as Source of Kaempferol in Rosemary Honey. *J. Sci. Food Agric.* **1998**, *77*, 506–510.
- (150) Bolzoni, L.; Careri, M.; Mangia, A. Characterization of Volatile Components in Apricot Purée by Gas Chromatography–Mass Spectrometry. *J. Chromatogr.* **1990**, *518*, 221–229.
- (151) Moret, I.; Gambaro, A. Trend Analysis in Selection of Aroma Components as Variables for Chemometric Studies of Typical Wines. *Ann. Chim.* **1996**, *86*, 309–318.
- (152) Chen, S. H.; Huang, T. C.; Ho, C. T.; Tsai, P. J. Extraction, Analysis and Study on the Volatiles in Roselle Tea. *J. Agric. Food Chem.* **1998**, *46*, 1101–1105.
- (153) Stremple, P. GC/MS Analysis of Polymethoxyflavones in Citrus Oils. *J. High Resolut. Chromatogr.* **1998**, *21* (11), 587–591.
- (154) Garcia-Jares, C.; Garcia-Martin, S.; Cela-Torrijos, R. Analysis of Some Highly Volatile Compounds of Wine by Means of Purge and Cold Trapping Injector Capillary Gas Chromatography. Application to the Differentiation of Rias Baixas Spanish White Wines. *J. Agric. Food Chem.* **1995**, *43*, 764–768.
- (155) Gomes da Silva, M. D. R.; Chaves das Neves, H. J. Differentiation of Strawberry Varieties Through purge-and-Trap HRGC-MS, HRGC–FTIR and Principal Component Analysis. *J. High Resolut. Chromatogr.* **1997**, *20*, 275–283.
- (156) Arena, E.; Campisi, S.; Fallico, B.; Maccarone, E. Fatty Acids of Italian Blood Orange Juices. *J. Agric. Food Chem.* **1998**, *46*, 4138–4143.
- (157) Gilbert, J.; Shepherd, M. J.; Wallwork, M. A.; Harris, R. G. Determination of the Geographical Origin of Honeys by Multivariate Analysis of Gas Chromatographic Data on their Free Amino Acid Content. *J. Apic. Res.* **1981**, *20* (2), 125–135.
- (158) Pérez-Arquillué, C.; Conchello, P.; Arino, A.; Juan, T. J.; Herrera, A. Physicochemical Attributes and pollen Spectrum of Some Unifloral Spanish Honeys. *Food Chem.* **1995**, *54*, 167–172.
- (159) Wilkins, A. L.; Lu, Y.; Tan, S. T. Extractives from New Zealand Honeys. 5. Aliphatic Dicarboxylic Acids in New Zealand Rewarewa (*Knigtea excelsa*) Honey. *J. Agric. Food Chem.* **1995**, *43*, 3021–3025.
- (160) D'Arcy, B. R.; Rintoul, G. B.; Rowland, C. Y.; Blackman, A. J. Composition of Australian Honey Extractives. 1. Norisoprenoids, Monoterpenes and other Natural Volatiles from Blue Gum (*Eucalyptus leucoxylon*) and Yellox Box (*Eucalyptus melliodora*) Honeys. *J. Agric. Food Chem.* **1997**, *45*, 1834–1843.
- (161) Lombard, A.; Buffa, M.; Patetta, A.; Manino, A.; Marletto, F. Some Aspects of the Carbohydrate Composition of Callaphidid Honeydew. *J. Apic. Res.* **1987**, *26* (4), 233–237.
- (162) Astwood, K.; Lee, B.; Manley-Harris, M. Oligosaccharides in New Zealand Honeydew Honey. *J. Agric. Food Chem.* **1998**, *46*, 4958–4962.
- (163) Pirini, A.; Conte, L. S.; Francioso, O.; Lercker, G. Capillary Gas Chromatographic Determination of Free Amino Acids in Honeys as a Means of Discrimination Between Different Botanical Sources. *J. High Resolut. Chromatogr.* **1992**, *15* (3), 165–170.

- (164) Ferreres, F.; Giner, J. M.; Tomas-Barberan, F. A. A Comparative Study of Hesperetin and Methyl Anthranilate as Markers of the Floral Origin of Citrus Honey. *J. Sci. Food Agric.* **1994**, *65*, 371–372.
- (165) Garcia-Jares, C.; Garcia-Martin, S.; Carro-Marino, N.; Cela-Torrijos, R. GC-MS Identification of Volatile Components of Galician (Northwest Spain) White Wines. Application to Differentiate Rias Baixas Wines from Wines Produced in Nearby Geographical Regions. *J. Agric. Food Chem.* **1995**, *69*, 175–184.
- (166) Maffei, M.; Mucciarelli, M.; Scannerini, S. Essential Oils from Achillea Species of Different Geographic Origin. *Biochem. Syst. Ecol.* **1994**, *22* (7), 679–687.
- (167) König, W. A.; Fricke, C.; Saritas, Y.; Momeni, B.; Hohenfeld, G. Adulteration or Natural Variability? Enantioselective Gas Chromatography in Purity Control of Essential Oils. *J. High Resolut. Chromatogr.* **1997**, *20*, 55–61.
- (168) Aparicio, R.; Morales, M. T.; Alonso, V. Authentication of European Virgin Olive Oils by Their Chemical Compounds, Sensory Attributes; Consumers' Attitudes. *J. Agric. Food Chem.* **1997**, *45*, 1076–1083.
- (169) Carrera, F.; Leon-Camacho, M.; Pablos, F.; Gonzalez, A. G. Authentication of Green Coffee Varieties According to their Sterolic Profile. *Anal. Chim. Acta* **1998**, *370*, 131–139.
- (170) Ng, L. K.; Hupé, M. Analysis of Sterols: a Novel Approach for detecting Juices of Pineapple, Passionfruit, Orange and Grapefruit in Compounded Beverages. *J. Sci. Food Agric.* **1998**, *76*, 617–627.
- (171) Low, N. H.; South, W. Determination of Honey Authenticity by Capillary Gas Chromatography. *J. AOAC Int.* **1995**, *78* (5), 1210–1218.
- (172) Piry, J.; Pribela, A.; Durcanska, J.; Farkas, P. Fractionation of Volatiles from Blackcurrant (*Ribes nigrum* L.) by Different Extractive Methods. *Food Chem.* **1995**, *54*, 73–77.
- (173) Mochizuki, E.; Yamamoto, T.; Komiyama, Y.; Nakasawa, H. Identification of Allium Products Using Flame Photometric Detection Gas Chromatography and Distribution Patterns of Volatile Sulfur Compounds. *J. Agric. Food Chem.* **1998**, *46*, 5170–5176.
- (174) Girard, B.; Kopp, T. G. Physicochemical Characteristics of Selected Sweet Cherry Cultivars. *J. Agric. Food Chem.* **1998**, *46*, 471–476.
- (175) Di Bella, G.; Saitta, M.; Pellegrino, M.; Salvo, F.; Dugo, G. Contamination of Italian Citrus Oils: Presence of Phthalate Esters. *J. Agric. Food Chem.* **1999**, *47*, 1009–1012.
- (176) Carstensen, J. T.; Van Scoik, K. Amorphous to Crystalline Transformation of Sucrose. *Pharm. Res.* **1990**, *7* (12), 1278–1281.
- (177) Te Booy, M. P. W. M.; de Ruiter, R. A.; de Meere, A. L. J. Evaluation of the Physical Stability of Freeze-Dried Sucrose-Containing Formulations by Differential Scanning Calorimetry. *Pharm. Res.* **1992**, *9* (1), 109–114.
- (178) Raemy, A.; Kaabi, C.; Ernst, E.; Vuataz, G. Precise Determination of Low Level Sucrose Amorphism by Microcalorimetry. *J. Therm. Anal.* **1993**, *40*, 437–444.
- (179) Arvanitoyannis, I.; Blanshard, J. M. V.; Ablett, S.; Izzard, M. J.; Lillford, P. J. Calorimetric Study of the Glass Transition Occurring in Aqueous Glucose:Fructose Solutions. *J. Sci. Food Agric.* **1993**, *63*, 177–188.
- (180) Wang, G. M.; Haymet, A. D. Trehalose and Other Sugar Solutions at Low Temperature: Modulated Differential Scanning Calorimetry (MDSC). *J. Phys. Chem. B* **1998**, *102*, 5341–5347.
- (181) Kantor, Z.; Pitsi, G.; Thoen, J. Glass Transition Temperature of Honey as a Function of Water Content as Determined by Differential Scanning Calorimetry. *J. Agric. Food Chem.* **1999**, *47* (6), 2327–2330.
- (182) Malisan, M.; Maltini, E. Comportamento Termico E Fisico di Miele Tipici. *Ind. Aliment.* **1999**, *38*, 549–559.
- (183) Simon, P.; Kolman, I.; Schmidt, S. Analysis of the Induction Period of Oxidation of Edible Oils by Differential Scanning Calorimetry. *J. Am. Oil Chem. Soc.* **2000**, *77* (6), 639–642.
- (184) Runge, F. E.; Heger, R. Use of Microcalorimetry in Monitoring Stability Studies. Example: Vitamin A esters. *J. Agric. Food Chem.* **2000**, *48*, 47–55.
- (185) Findlay, C. J.; Barbut, S.; Harwalkar, H. Thermal Analysis of Meat. In *Thermal Analysis of Foods*; Elsevier: Amsterdam, The Netherlands, 1990; pp 92–98.
- (186) Tocci, A. M.; Mascheroni, R. H. Characteristics of Differential Scanning Calorimetry Determination of Thermophysical Properties of Meats. *Lebensm. Wiss. -Technol.* **1998**, *31*, 418–426.
- (187) Acquistucci, R.; Bucci, R.; Magri, A. D.; Magri, A. L. Thermal Analysis of Food Carbohydrates by Determination of Starch Gelatinization Phenomena. *Fresenius' J. Anal. Chem.* **1997**, *357*, 97–100.
- (188) Breitschuh, B.; Windhab, E. J. Direct Measurement of Thermal Fat Crystal Properties for Milk-Fat Fractionation. *J. AOAC Int.* **1996**, *73* (11), 1603–1610.
- (189) Chevallier, S.; Colonna, P.; Della Valle, G.; Lourdin, D. Contribution of Major Ingredients During Backing of Biscuit Dough Systems. *J. Cereal Sci.* **2000**, 241–252.
- (190) Chevallier, S.; Colonna, P.; Buléon, A.; Della Valle, G. Physicochemical Behaviour of Sugars, Lipids; Gluten in Short Dough and Biscuit. *J. Agric. Food Chem.* **2000**, *48* (4), 1322–1326.
- (191) Lai, Y. W.; Kemsley, K.; Wilson, R. H. Potential of Fourier Transform Infrared Spectroscopy for the Authentication of Vegetable Oils. *J. Agric. Food Chem.* **1994**, *42*, 1154–1159.
- (192) Defernez, M.; Kemsley, E. K.; Wilson, R. H. Use of Infrared Spectroscopy and Chemometrics for the Authentication of Fruit Purees. *J. Agric. Food Chem.* **1995**, *43*, 109–113.
- (193) Kemsley, E. K.; Holland, J. K.; Defernez, M.; Wilson, R. H. Detection of Adulteration of Raspberry Purees Using Infrared Spectroscopy and Chemometrics. *J. Agric. Food Chem.* **1996**, *44*, 3864–3870.
- (194) Twomey, M.; Downey, G.; McNulty, P. B. The Potential of NIR Spectroscopy for the Detection of the Adulteration of Orange Juices. *J. Sci. Food Agric.* **1995**, *67*, 77–84.
- (195) Downey, G.; Boussion, J. Authentication of Coffee Bean Variety by Near-Infrared Reflectance Spectroscopy of Dried Extract. *J. Sci. Food Agric.* **1996**, *71*, 41–49.
- (196) Downey, G.; Briandet, R.; Wilson, R. H.; Kemsley, E. K. Near- and Mid-Infrared Spectroscopies in Food Authentication: Coffee Varietal Identification. *J. Agric. Food Chem.* **1997**, *45*, 4357–4361.
- (197) Ding, H. B.; Xu, R. J. Near-infrared spectroscopic technique for detection of beef hamburger adulteration. *J. Agric. Food Chem.* **2000**, *48* (6), 2193–2198.
- (198) Zamora, R.; Alba, V.; Hidalgo, F. J. Use of High-Resolution <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy for the Screening of Virgin Olive Oils. *J. AOAC Int.* **2001**, *78* (1), 89–94.
- (199) Li, W.; Goovaerts, P.; Meurens, M. Quantitative Analysis of Individual Sugars and Acids in Orange Juices by Near-Infrared Spectroscopy of Dry Extract. *J. Agric. Food Chem.* **1996**, *44*, 2252–2259.
- (200) Suchanek, M.; Filipova, H.; Volka, K.; Delgadillon, I.; Davies, A. N. Qualitative Analysis of Green Coffee by Infrared Spectroscopy. *Fresenius' J. Anal. Chem.* **1996**, *354*, 327–332.
- (201) Kemsley, E. K.; Ruault, S.; Wilson, R. H. Discrimination between *Coffea arabica* and *Coffea canephora* variant *robusta* beans using Infrared Spectroscopy. *Food Chem.* **1995**, *54*, 321–326.
- (202) Liu, Y.; Chen, Y.-R.; Ozaki, Y. Two-Dimensional Visible/Near-Infrared Correlation Spectroscopy Study of Thermal Treatment of Chicken Meats. *J. Agric. Food Chem.* **2000**, *48*, 901–908.

---

Received for review August 13, 2001. Revised manuscript received January 1, 2002. Accepted January 7, 2002.