Authentication and Traceability of Agricultural and Food Products Using Vibrational Spectroscopy

Philippe Vermeulen, Juan Antonio Fernández Pierna, Ouissam Abbas, Pierre Dardenne and Vincent Baeten

Walloon Agricultural Research Centre (CRA-W), Gembloux, Belgium

1 INTRODUCTION

The behavior of European consumers has been undergoing gradual changes. People require not only high-quality, safe products (dietary, hygienic, and health standards) but also certification and reassurance on a product's origin and production methods.[1] In order to preserve quality food products coming from particular geographical areas and to protect consumers against imitations and false information, the European Commission (EC) defined, via Regulations 509/2006[2] and 510/2006,[3] the labels Traditional Speciality Guaranteed (TSG), Protected Designation of Origin (PDO), and Protected Geographical Indication (PGI). The PDO label covers agricultural products and foodstuffs that are produced, processed, and prepared in a given geographical area using recognized expertise. The PGI label covers agricultural products and foodstuffs for which at least one of the stages of production, processing, or preparation takes place in the given area. The TSG label highlights traditional character, either in the composition or in the means of production. To date, 680 PDO, 560 PGI, and 44 TSG products have been registered[4]; these are mainly European products but also include coffee from Colombia, spices from China, and tea from India. In 2006, a European logo was introduced in order to identify agricultural products from the overseas regions (i.e., European Union (EU) regions not located on the European continent). Also, a European organic farming logo was created to cover goods produced mainly from ingredients of organic agricultural origin. It gives consumers confidence about the origins and quality of their food in compliance with European organic farming regulations.[5] This logo will become mandatory from July 1, 2010. National labels are also applied, such as the *Appellation d'origine contrôlée* (*AOC*) used in France, the *Denominazione di origine controllata* (*DOC*) in Italy, and the *Denominación de Origen* (*DO*) in Spain. Quality labels play an important role in consumer behavior, with

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people buying these products because of their reputation.

Traceability is an essential tool to enhance trader and consumer confidence in the safety, quality, and authenticity of the food. It also helps the regulatory authorities to detect fraud and dangerous substances. According to Regulation EC 178/2002[6] of the EC, the term *traceability* means the ability to trace and follow a food, feed, and food-producing animal or substance intended or expected to be incorporated into a food or feed, through all stages of production, processing, and distribution. This EU directive came into effect on January 1, 2005 and requires mandatory traceability for all food and feed products sold within EU countries. Traceability with regard to authenticity issues can be interpreted as verifying the labels previously defined, tracing the origin of food or confirming the presence of ingredients claimed to be in that food. A number of questions arise when the issues of food traceability and authentication are discussed. These include the following:

(i) Is the food typical of the type of food which it claims to be? In other words, can it be confirmed to be the same as what is declared on the label with a high degree of certainty?
(ii) Is the food typical of the batch of products from which it came? In other words, can it be confirmed that the food was not subject to post-production changes?
(iii) If the answer to either of these questions is "No", then can the nature of the mislabeling, fraud, or change be identified?

Today, food traceability procedures often involve tedious administrative documents. Scientific parameters that objectively identify a product would be preferable. Scientific research in this area is focused mainly on developing analytical methods to authenticate the geographical origin of food,[7] and also to monitor possible changes in food properties during storage, distribution, and up to the point of retail sale (i.e., degradation and aging over time). Several projects on food and feed traceability have been funded by the EC that include analytical tools, traceability systems in industry, and consumer aspects.

The use of vibrational spectroscopy in traceability helps in authenticating the geographical origin, the variety/species origin, and the production process of food and feed products. Vibrational spectroscopic techniques allow the organic compounds present in agricultural products to be measured. These organic compounds absorb radiation at particular wavelengths (or wavenumbers), producing spectral signatures that are characteristic of the food/feed chemical composition and that could be considered as their *fingerprints*. The acquired signatures also include interferences due to variation occurring as a result of natural events (e.g., weather, climate, and disease) during the growth or production of primary foods, and as a result of batch-to-batch variations in processed agricultural products or food/feed ingredients. The large spectra databases obtained using the vibrational methods need chemometric techniques to detect primary food/feed that is not what it claims to be or processed agricultural products that do not conform to a declared specification. Supervised chemometric techniques such as soft independent modeling of class analogy (SIMCA), factorial discriminant analysis (FDA), linear discriminant analysis (LDA), stepwise linear discriminant analysis (SLDA), partial least squares discriminant analysis (PLS-DA), and support vector machines (SVM) among others have been applied, depending on the study, in order to develop classification rules. Representative samples of each group (known beforehand) are available, from which the relevant characteristics (e.g., designation of origin, country, variety, species) are known. Using these data, classification rules that can then be used to classify new (unknown) samples are determined.

Near-infrared (NIR), mid-infrared (mid-IR), and Raman spectroscopic methods have been or are being developed in order to assess authenticity issues. In the following sections of this chapter, several examples are discussed to illustrate the potential of vibrational spectroscopy to tackle authenticity challenges. Many of these are from European projects dealing

with authenticity: TYPIC (2001–2004, (http://www.typic.org/)[8] that aimed to assess the typicality of food; MEDEO (http://huespedes.cica.es/aliens/igmedeo/index.htm)[9] that aimed to detect hazelnut oil in olive oil; TRACE (http://www.trace.eu.org/) that focused on the authentication and traceability of foods produced in defined geographical areas or using specific production methods[10]; FONIO (http://inco-fonio-en.cirad.fr/fonio_project) that dealt with the identification of different origins and varieties of a certain traditional cereal[11]; CO-EXTRA (http://www.coextra.eu/) that aimed to detect genetically modified material[12]; SAFEED-PAP (http://safeedpap.feedsafety.org/) that focused on the detection and identification of species-specific animal proteins in feed,[13] and CON*ff*IDENCE (http://www.conffidence.eu/) that aimed to detect contaminants in food and feed.[14] However, the methods and results could be extended and applied to agricultural and food product issues from other parts of the world. Nevertheless, the reader will find several bibliographic references regarding studies carried out outside Europe.

2 AUTHENTICITY AND TRACEABILITY ISSUES: FOOD AND FEED EXAMPLES

2.1 Authentication and typical assessment of meat and meat products

Several methods have been published in the literature for the authentication of meat and meat products.[15] Near-infrared spectroscopy (NIRS) provides a fast and nondestructive way to assess intrinsic meat quality by determining the concentration of major compounds such as water, proteins, and lipids.[16,17] NIRS also has strong potential for estimating some physicochemical properties of meat, such as collagen content, juiciness, and tenderness,[18] partially linked to the organoleptic quality. Other studies have shown that NIRS applied to muscle analysis is an efficient tool for identifying animal species,[19,20] and it can also be used to identify beef muscle samples according to their feeding regime.[21] With regard to chicken meat, Fumière *et al.*[22] described the use of NIRS to discriminate slow-growing-strain chickens from chickens belonging to strains selected for their high feed efficiency and fast growth rate. Ding *et al.*[23] discriminated the Shek-kei chicken breed (a high-quality breed) from other local chickens. NIRS has also been employed to discriminate between kangaroo and beef meat[24]; fresh pork, chicken, and turkey[25]; chicken meat cuts[22,23]; lamb and beef mixtures[26]; and also beef, pork, and chicken,[27] in addition to the authentication of raw meat species as pork, lamb, beef, and chicken,[19] and the differentiation between fresh and frozen-then-thawed bovine meat.[28] The latter study has been followed by another one based on the dried meat drip juice,[29] which permits a better classification of fresh and frozen-then-thawed meat.

The TYPIC European project,[8] in which the CRA-W (Walloon Agricultural Research Centre, Belgium) research team was involved, sought, among other things, to assess the typicality of dry-cured hams by NIRS. Forty-one dry-cured hams (20 from various regions in France and 21 from various regions in Spain) under DO and other labels across the EU, as well as from different breeds, were selected by food chain experts and trained sensory panels external to the food chain. For each sample, the mixture obtained was divided into five subsamples, which were put into five NIRS reflection cells and analyzed. The reflection cell was a circular aluminum cup covered with a slide glass (crystal or quartz). The back of the cup was sealed with a piece of cardboard protected with a cellophane film. Spectra were acquired in reflection mode and each spectrum was the mean of 32 scans. The IR radiation covered by the spectrum ranged from 400 to 2500 nm with a 2-nm step. Data collection was performed using a spinning configuration (i.e., the sample holder was turned during analysis). Various chemometric tools (PCA, PLS-DA, and SVM) were used in order to classify

hams according to their country of origin, region, breed, and maturation time. For all these studies, discrimination models were constructed on a calibration set and validated using an independent test set. For the classification of hams according to the country of origin, 95% of the samples in the test set were correctly classified by PLS-DA. When studying the classification of hams according to region of origin, SVM were used to discriminate the typical hams from the nontypical samples for the same country (Figure 1). A correct classification of 75% and 79% for French hams and Spanish hams, respectively, was obtained for the independent test set. For breed, a correct classification rate of 100% was obtained. This study showed that the combination of chemometric methods with NIRS could be used to classify hams according to some qualitative and sensory characteristics related to the typicality of dry-cured hams (origin, breed, acorn flavor, sheen, etc.).

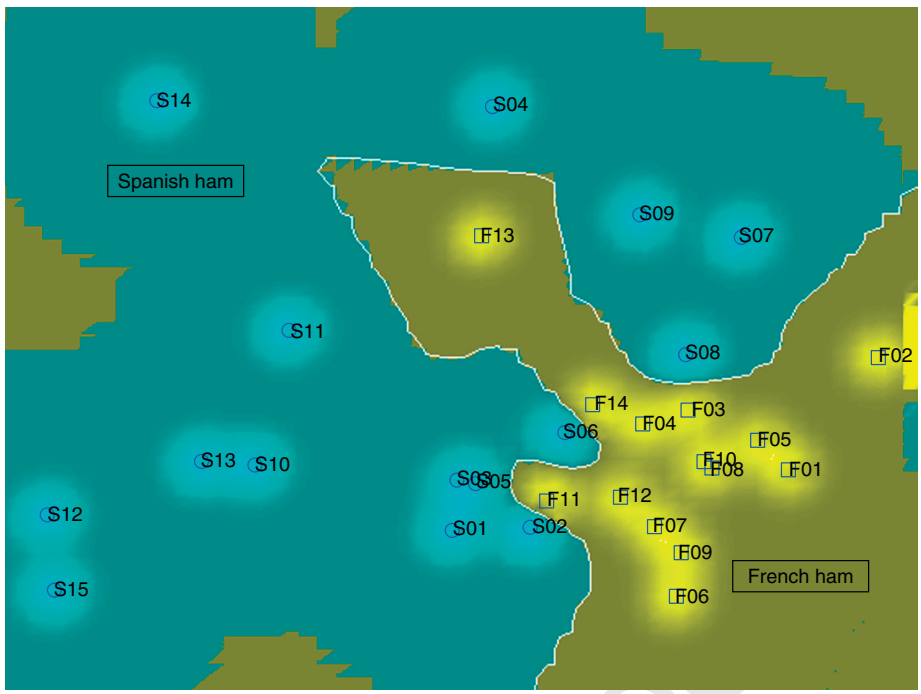
The potential of mid-IR spectroscopy to differentiate between turkey, chicken, and pork meats has been shown by Al-Jowder *et al.*[30] by applying PCA; moreover, they also succeeded in discriminating between fresh and frozen-then-thawed meat samples. In another study, they have shown[31] the possibility of using mid-IR attenuated total reflection (ATR) spectroscopy to detect adulteration of raw ground beef with offal obtained from the same species, particularly kidney and liver, which have lower fat content; besides, liver samples contain appreciable levels of glycogen. Another study undertaken by the same group[32] demonstrated the ability of mid-IR ATR spectroscopy to distinguish between pure beef and beef containing 20% of heart, tripe, kidney, or liver with a 97% correct classification rate; both raw and cooked samples in different regimes of cooking were studied. Mid-IR spectroscopy has also been used to detect the addition of proteolytic enzymes from plants, used as meat tenderizers. Lizuka and Aishima[33] applied mid-IR spectroscopy to differentiate between reference beef and beef treated with pineapple juice. Adhikari *et al.*[34] applied mid-IR spectroscopy to detect the presence of and changes in the levels of hexanal and methyl sulfide in meal, ready-to-eat (MRE) omelettes with ham.

Raman spectroscopy has also been used for the study of meat. Discrimination between chicken and turkey meat was attempted by Raman spectroscopy on the basis of analysis performed on breast and leg muscles; however, the major discrimination was due to the different biochemical nature of the muscle types, and smaller differences were due to meat species.[35]

2.2 Authentication and typicality assessment of alcoholic beverages

NIRS has been widely used in the quality assessment of wine and grapes. Arana *et al.*[36] used NIRS to determine the soluble solids content and identify grape varieties and origins. Samples of Viura and Chardonnay grapes were collected from two locations with different environmental conditions. The results of discriminant analysis using specific variables from the NIR spectrum showed 97.2% correct classification of grapes according to the variety and 79.2% correct classification of grapes according to the location. Cozzolino *et al.*[37] have used NIRS coupled to PLS-DA to successfully discriminate the origin of two varieties of Australian white wines—Riesling and Chardonnay. Yu *et al.* have used Fourier transform near-infrared spectroscopy (FT-NIRS) to discriminate the geographic origin and the age of Chinese rice wine,[38,39] and to predict the vintage year of Chinese rice wine.[40] Pontes *et al.*[41] have proposed using FT-NIRS coupled with the chemometric tools PCA and SIMCA to classify and check the adulteration of whiskeys, brandies, rums, and vodkas.

The wine industry needs robust and rapid methods to ensure the quality of the product delivered to the consumer. Mid-IR spectroscopy may be used as a fingerprint method for wine products. Bevin *et al.*[42] applied mid-IR spectroscopy to discriminate 161 Australian wine samples coming from three grape varieties and collected from six commercial wineries. Spectra



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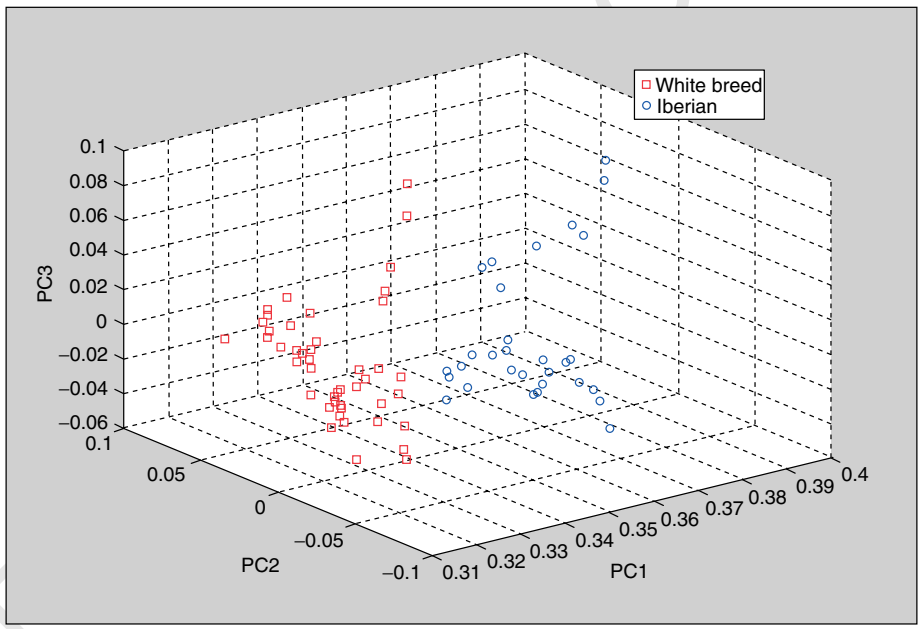

(b)

Figure 1. Results of NIR spectroscopy with: (a) SVM for the discrimination between French and Spanish hams; and (b) PCA analysis for the discrimination between the different breeds: white breed (red squares) and Iberian breed (blue circles).

were collected in the transmission mode before and after transportation in order to assess any changes that had occurred. Because water is present at 85–90% of the wine matrix, they suggested subtraction of its relevant bands and applied a PLS regression, which permits a good prediction of the similarity index. A similar study was previously undertaken by using mid-IR spectroscopy to discriminate Austrian red wines of different cultivars.[43] The discrimination of red wines according to their geographical origin and vintage was investigated by Picque *et al.*[44] The PLS-DA model built on dry extracts of wines from different areas over 4 years showed 92 and 85% rates of correct classification for a validation set for the vintage and the geographical origin sets, respectively. A conclusion from this study is that phenolic compounds seem to be significant for the discrimination of the red wines. Picque *et al.*[45] have also studied the potential of mid-IR spectroscopy to differentiate Cognac and other distilled drinks like whiskeys, rums, brandies, Armagnacs, bourbons, and counterfeit products, on the basis of spectra of their dried and phenolic extracts. Edelmann *et al.*[43] used the mid-IR spectroscopic range to discriminate between several Austrian red wine cultivars. Phenolic extracts obtained by the solid-phase-extraction (SPE) technique were selected to perform the discrimination. The combination of the SPE, mid-IR spectroscopy, and chemometrics allowed the cultivars Cabernet Sauvignon, Merlot, Pinot Noir, Blaufränkisch (Lemberger), St Laurent, and Zweigelt to be identified.

A study has also been performed by the CRA-W research group within the framework of the TYPIC project, focusing on a collection of 120 red wines from Germany and France. For each wine, two vintages were studied. The French wines consisted of 20 typical Beaujolais wines (from the Beaujolais region) and 10 wines from other regions (outsiders). The German wine group contained 24 typical Dornfelder wines from the Pfalz region and 6 from outside. IR spectra were acquired with a Fourier transform infrared (FT-IR) spectrometer equipped with a temperature stabilization system and a DTGS detector (*see* **Introduction to the Theory and Instrumentation for Vibrational Spectroscopy**). The samples were analyzed in transmission mode with a specially designed flow cell (16-μm path length). The resolution was 4 cm^{-1} and each spectrum was an average of 50 scans. The spectra ranged from 4000 to 600 cm^{-1} with an interval of 2 cm^{-1}. Multivariate methods such as SVM or PLS-DA showed that almost 80% of the wines could be correctly classified according to the country of origin and even greater discrimination could be achieved with the different cultivars (Figure 2). The study also showed that some enological patterns can be calibrated and predicted using mid-IR spectroscopy.

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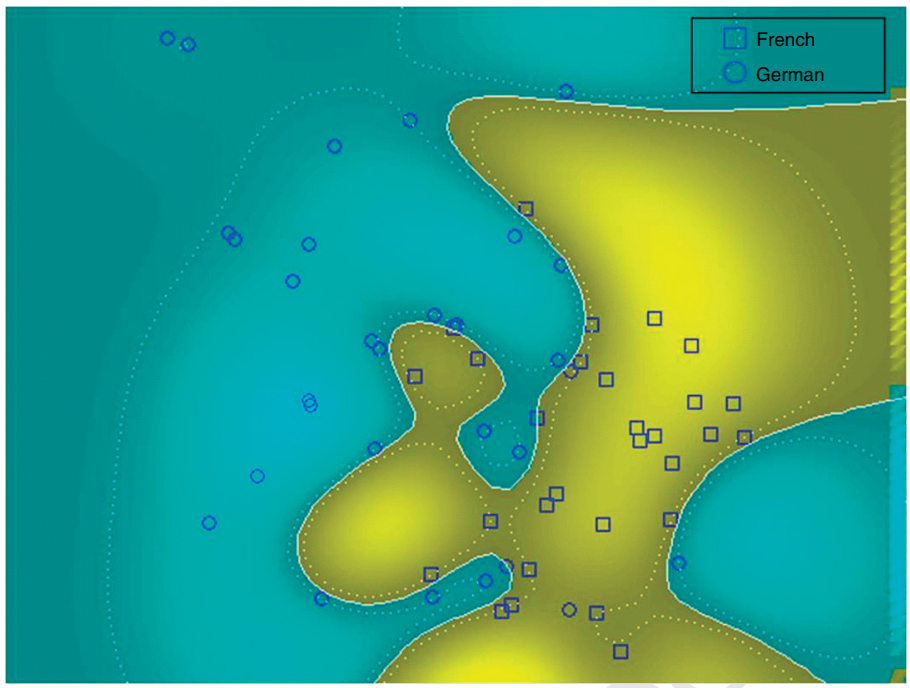
Raman spectroscopy has been used to study the hydrogen-bonding properties of water–ethanol in alcoholic beverages[46–48]; the ratio of peak intensities at 3200 and 3400 cm^{-1} allows one to estimate the degree of the hydrogen-bonding strength of water–ethanol mixtures. Raman spectroscopy has also been used to analyze the alcohol content of different types of alcoholic beverages (whiskey, vodka, and sugary drinks) on the basis of the signal at 880 cm^{-1} associated with the symmetric C–C–O stretching vibration.[49] The researchers established univariate models covering percentages of ethanol between 19.2 and 61.7 (v/v), with an accuracy of 0.5%. Those models can help detect fraudulent practices by some beverage producers.

Beer is an economically important product of cereal fermentation. In Belgium, beers from Trappist monasteries enjoy particular status because of their perceived high and consistent quality. To protect this status and as an aid to marketing, beers brewed in monastic sites under the control of Trappist monks are entitled to display a Trappist logo on their label. Of the world's 171 Trappist monasteries (as of April 2005), seven produce beer—six in Belgium (Orval, Chimay, Westvleteren, Rochefort, Westmalle, and Achel) and one in The Netherlands (La Trappe). Within the framework of the TRACE project, several spectroscopic fingerprint techniques have been deployed to develop models that would confirm the identity of Trappist beers. A set ($n = 124$)



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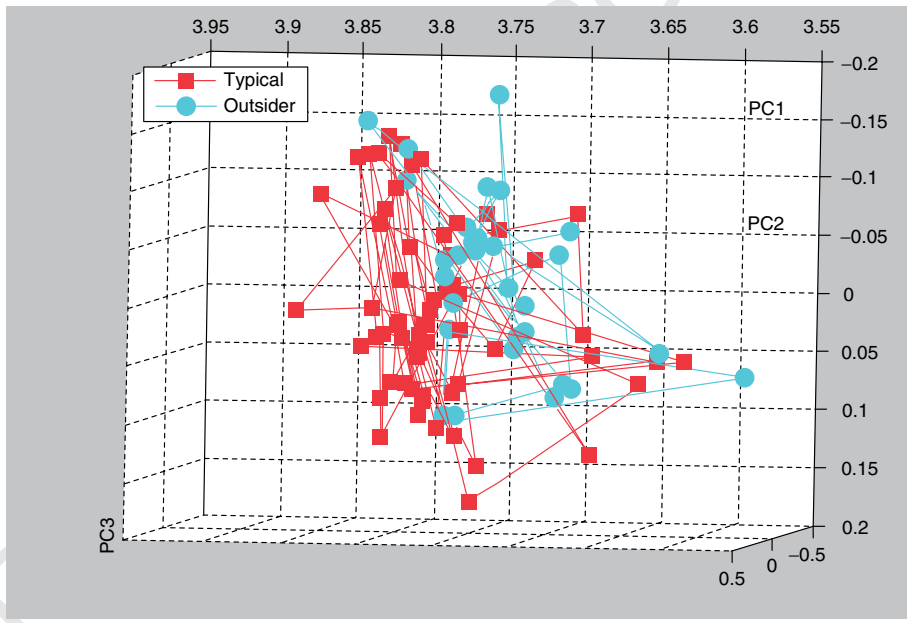


(b)

Figure 2. Results of mid-IR spectroscopy with: (a) SVM for the discrimination between French (blue squares) and German (blue circles) wines; and (b) PCA analysis for the discrimination between typical Beaujolais wines (red filled squares) and wines from other regions, called outsiders (blue filled circles).

of Trappist and non-Trappist beers was collected from several production batches and analyzed. Chemometric models were developed to discriminate between Trappist and non-Trappist beers. A second set of beers ($n = 124$) was collected from different batches of beers on a second occasion to evaluate the accuracy of previously developed discriminant models and to determine the stability of the models when applied to beers that had been stored for an extended time. Various PCA models were constructed according to the degree of alcohol and color, as well as their membership of the group of Trappist beers, especially Rochefort beer (Figure 3). PLS-DA models were then constructed in order to discriminate (i) Trappist beers from the rest of the beers, (ii) Rochefort from the other beers, and (iii) Rochefort 8 from the rest. For all these models, the results were expressed in terms of correct classification, as well as false positive and false negative rates. In all the cases studied, reasonable classification rates (>90%) were obtained, showing the ability of FT-Raman spectroscopy and chemometrics to authenticate beers.[50] The NIR and mid-IR results indicate the potential of these techniques to discriminate Rochefort from the other beers with a correct classification of 78.6% and 89.7%, respectively, and to discriminate Rochefort 8 from the rest with 100% correct classification for both techniques.[51]

2.3 Authenticity and adulteration detection of edible oils and fats

Because of the interesting nutritional properties and economic value of some oils, like olive oil, the added-value products can be the subject of an adulteration or a fraud. For this purpose, several studies have been performed applying vibrational spectroscopy to study the discrimination, adulteration, and/or composition of vegetable oils.

Application of NIRS to oils and fats was first employed for qualitative studies; it was proposed to build a library of NIR spectra of fats in order to detect a spectral match of an unknown sample,[52] and to distinguish vegetable oils using discriminant analysis.[53,54] Hourant *et al.*[55] have used NIRS to discriminate fats and oils from different vegetable and animal sources; the classification has been made using a tree structure based on SLDA from 104 edible oil and fat samples from 18 different sources, the fatty acid contents of which had been analyzed by high-performance gas chromatography. Another important application of NIRS is in the quality control of olive oil known for its high nutritional value. Wesley *et al.*[56,57] have treated NIR spectral data by PCA and by the development of a discriminant equation which permits one to first detect and then quantify adulterants in olive oil with an accuracy of ±0.9%. Similarly, Downey *et al.*[58] have first applied SIMCA on NIRS-collected data in order to discriminate authentic extra-virgin oils from those adulterated by sunflower oil at a level of 1% (w/w), and then they have applied a PLS regression to quantify the adulterant content.

Several studies on the use of FT-NIRS have been carried out in order to analyze edible oils.[59–62] These have analyzed the peroxide value, cis and trans fatty acid content, iodine value, saponification number, and also discrimination of these oils. Recently, the ability of FT-NIRS to rapidly classify edible oils and fats has been confirmed by Yang *et al.*[63] through a study to determine olive pomace oil adulteration in extra-virgin olive oil. Other studies concerned with the adulteration of vegetable oils include the use of FT-NIRS, which has been combined with PLS regression to detect and quantify the adulteration of olive oils by corn, hazelnut, sunflower, and soya oils,[64] and its coupling to chemometric tools for the detection of diesel/biodiesel in vegetable oils.[65]

Mid-IR spectroscopy has played an important role in the quality assessment of fats and edible oils. The quantitative determination of peroxide value (PV) of vegetable oils by mid-IR spectroscopy has been realized by Van de Voort *et al.*[66] Calibration samples were prepared so that they had different PVs, and then a PLS regression was applied to the 3750–3150 cm^{-1} region. Results were compared with reference values obtained by

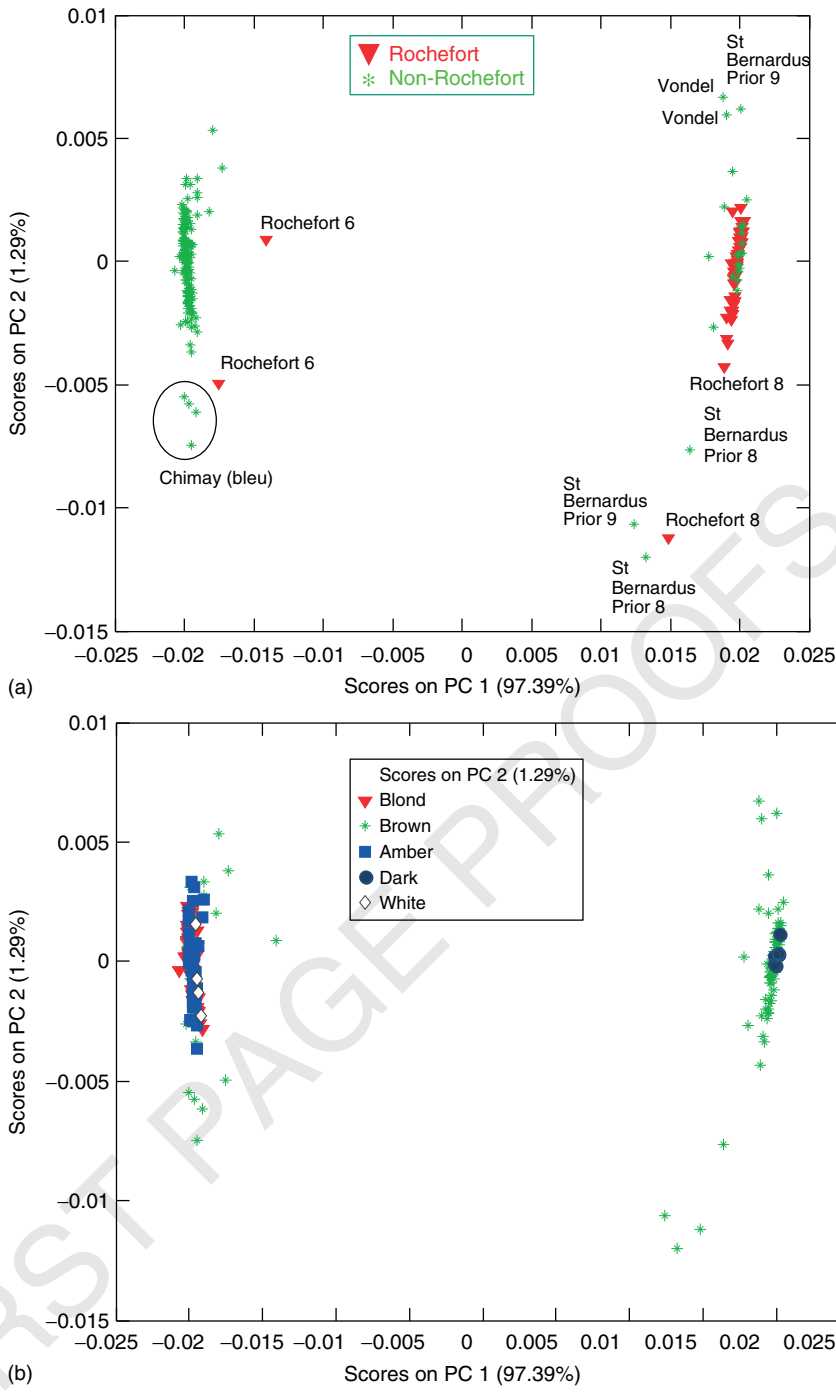


Figure 3. (a) PCA results of FT-Raman spectra for the discrimination between Rochefort and non-Rochefort beers; (b) PCA analysis of FT-Raman spectra for the discrimination according to the color of the beers: blond (red inverted triangles), brown (green asterisks), amber (blue filled squares), dark (dark blue filled circles), and white (white diamonds).

chemical methods. The same group has worked on the determination of cis and trans contents of edible oils,[67] where a mid-IR spectroscopy PLS method was revealed to be an efficient means to determine a wide range of trans content. A similar study has been carried out by Guillèn and Cabo.[68] Marigheto *et al.*[69] have evaluated the ability of mid-IR spectroscopy to discriminate oils from different botanical sources, and to detect added adulterants. The 140 spectra of pure oils were divided into calibration ($n = 84$), validation ($n = 27$), and prediction ($n = 29$) sets. Some samples were then adulterated at different levels. Results indicated a correct classification of 100% of oil samples when applying LDA or an artificial neural network (ANN) procedure. This result was later confirmed by Tay *et al.*[70] and Inón *et al.*,[71] who demonstrated the ability of mid-IR spectroscopy to discriminate extra-virgin olive oil from adulterated oil. In another study, the potential of mid-IR spectroscopy was evaluated to distinguish sources of fats used in feedstuff formulations, mainly to differentiate between tallow (ruminant fat) and nonruminant fat.[72] Results showed quite a good discrimination of pure fat samples, but a limited ability to define animal species and fat classes. Gasperini *et al.*[73] applied transmission mid-IR spectroscopy recorded from thin layers to classify food oil co- and by-products used in feed preparation.

FT-Raman spectroscopy has been successfully investigated for rapid detection of adulteration of oils and fats. Adulteration of virgin olive oil with olive pomace oil has been studied by discriminating the oils on the basis of the vibrations of unsaturated groups, as shown in recorded FT-Raman spectra.[63] Recently, the technique has been applied on animal fats[74] and coupled to PLS-DA in order to discriminate animal fats belonging to different origins and fats from various types of feedstuff and industrial processes.

One of the most frequent adulterations of olive oil is the addition of hazelnut oil (*Corylus avellana* L.). The similar chemical composition of these oils makes this fraudulent practice potentially undetectable with current official methods. The nonexistence of official analytical methods for the detection of olive oil adulteration with hazelnut oils and the fact that consumers are very sensitive to mislabeling linked to adulterations are the two main motivations for several EC services and international institutions to have become involved in fraud prevention and detection in the olive oil sector. Baeten *et al.*,[75] within the framework of the MEDEO project, conducted a comprehensive study involving both qualitative and quantitative analyses for the detection of hazelnut oil in olive oil using mid-IR and FT-Raman spectroscopy. In qualitative analysis, discrimination between pure olive oil and hazelnut oil or between different olive oil categories was realized in order to detect adulteration. The quantitative analysis consisted of constructing different models to be used for the prediction of new samples. These models were based on the predictive ability of lipid and unsaponifiable fractions. First, a rule consisting of the ratio at different wavelengths was proposed to distinguish genuine hazelnut oils from genuine olive oils. The results obtained with this rule showed that the mid-IR spectra of the unsaponifiable matter discriminated between olive and hazelnut oil samples. Multivariate analyses were carried out by SLDA, which involved the construction of discriminant equations based on the spectral information at discrete frequencies. For each spectral library constructed with the training samples, different SLDA discriminant models were built to discriminate between genuine hazelnut oils, genuine olive oils, and their mixtures. The percentages of correct classification using mid-IR data for the genuine olive oils, genuine hazelnut oils, and their mixture samples were 85.7%, 100%, and 86.7%, respectively. The SLDA model based on the FT-Raman spectra of the unsaponifiable matter selected Raman scattering intensities at seven different Raman shifts. These Raman shifts belong to the 2950–3010-cm^{-1} region that contains vibrations characteristic of unsaturated groups, and the 1674–1663 cm^{-1} region, which has been attributed to the presence of squalene; squalene is a hydrocarbon that distinguishes hazelnut oil from olive oil.[76] The classification results showed that 95.0%, 100%, and 97.5%

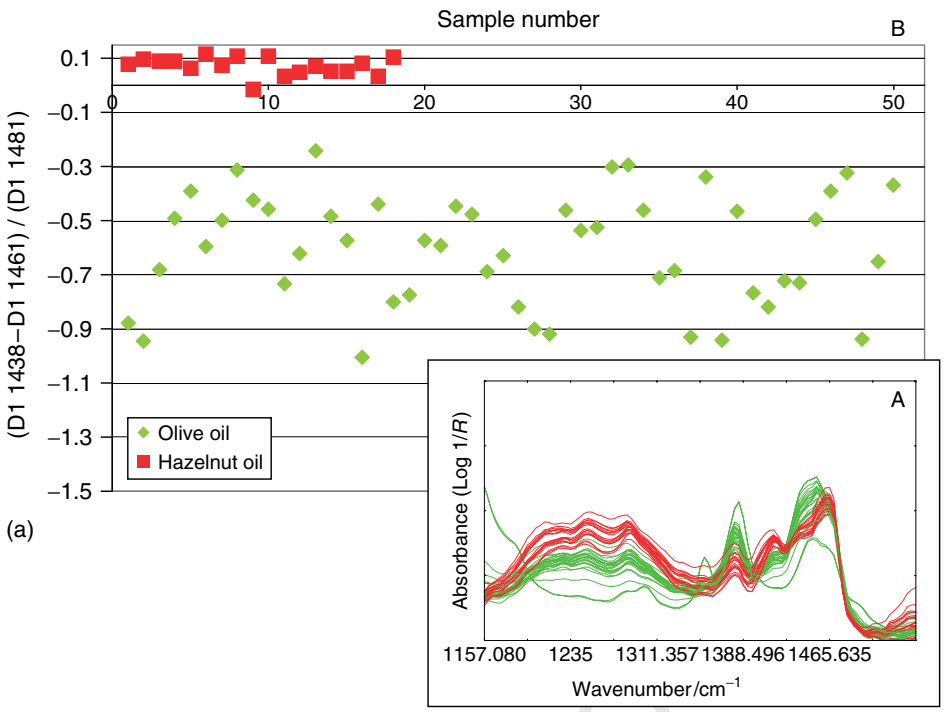
of the genuine olive oils, genuine hazelnut oils, and their mixtures were classified, respectively. The next step was to validate the SLDA models with 44 blind samples as well as other genuine olive and hazelnut oils. The described Raman and mid-IR spectroscopic models were checked with the spectra of the entire oil and its unsaponifiable matter. The best results were obtained with the mid-IR spectra of the unsaponifiable matter samples, although a few false positives were detected (Figure 4). The mid-IR spectra of the unsaponifiable samples allowed for discrimination between the pure olive oil samples and most of the adulterated samples.

Apart from fraud by adulteration, fraud regarding product origin is a second main concern for olive oil. The PDO regulations permit the labeling of some European extra-virgin olive oils with the names of the areas in which they are produced. This certification increases the commercial value of the product, and for this reason the possibility of fraudulent labeling of foods is a serious regulatory issue. The EU TRACE project is aimed to develop analytical procedures that are able to confirm the validity of any such labeling claim. Among the fingerprinting methods, NIR, mid-IR, and FT-Raman spectroscopies have been applied to the problem of confirming that olive oil labeled as being from the Italian region of Liguria conforms to a relevant specification. The overall objective was to derive a general methodology for authenticating products from all PDO and PGI regions. The samples ($n = 668$) had six origins: Italy, Spain, France, Greece, Cyprus, and Turkey; they were collected over two harvests. For each country, several samples from different regions, as well as different designations of origin, were included in the data set. The samples were analyzed using the spectroscopic techniques, and chemometric models were developed. Supervised techniques such as PLS-DA or SVM were applied in order to develop classification rules. The most accurate multivariate models for each analytical method were described and compared on the basis of sensitivity (% of actual Ligurian oils identified as Ligurian) and selectivity (% of non-Ligurian correctly identified as non-Ligurian). Results for sensitivity of 89.4%, 78.7%, and 82.3% and for selectivity of 84.5%, 79.3%, and 63% were obtained using NIR, mid-IR, and FT-Raman methods, respectively.[77–79]

2.4 Authentication of honey and other sweeteners

Honey is one of the most complex foodstuffs produced by nature and certainly the only sweetening agent that can be used by human beings without processing. In recent years, the characterization of both chemical and sensory characteristics of honey has received increasing attention. Quality control methods, in conjunction with multivariate statistical analysis, have been shown to be able to classify honey according to different geographical regions, adulteration, and chemical characteristics. Traditionally, the determination of the floral origin of honey has been achieved by palynological analysis. These methods are based on the identification of pollen by microscopic inspection, which is a difficult task. A South American study has reported the use of visible and NIR spectroscopies to classify honey samples from Uruguay, according to their floral origin.[80] Honey samples ($n = 50$) from two floral origins, namely, *Eucalyptus* spp. and pasture, were collected. On average, LDA and PLS-DA models correctly classified more than 75% of the honey samples from pasture and more than 85% of the honey samples from *Eucalyptus* spp. NIRS has been widely employed to study the chemical composition of honey samples[81–84] and to detect the adulteration of Irish artisanal honeys by adding either beet invert syrup or high-fructose corn syrup. FT-NIRS studies have focused on the botanical origin of honey.[85] The potential of the method has been tested on unifloral and multifloral honey samples originating from Switzerland, which were analyzed and classified by PCA, PLS-DA, and LDA methods.

Mid-IR spectroscopy combined with chemometric analysis has been revealed to be a good tool to predict glucose, fructose, and



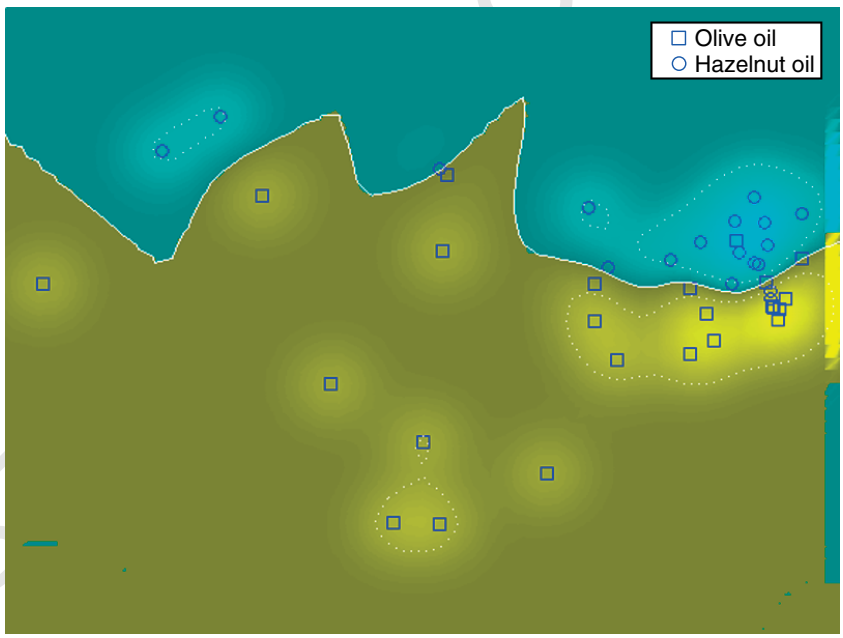


Figure 4. (a) Mid-IR spectra of unsaponifiable matter (A) and value of the applied rules to discriminate between olive and hazelnut oils (B): olive oil (green diamonds and green spectra), hazelnut oil (red squares and red spectra); (b) SVM results for the discrimination between olive and hazelnut oils.

sucrose in aqueous mixtures of 10, 20, and 40% of total sugar with coefficient of determination, R^2, values of 0.997, 0.998, and 0.997, respectively.[86] Paradkar *et al.*[87] have also shown the ability of mid-IR and NIR spectroscopies to detect the adulteration of maple syrup with additives like cane and beet sugar solutions. The spectral regions corresponding to carbohydrates ($1200-800\,cm^{-1}$), organic acids ($1800-1200\,cm^{-1}$), and amino acids ($3200-2800\,cm^{-1}$) can be considered as good markers to detect the adulterant in maple syrup.[88] Maalouly *et al.*[89] have carried out a similar study to detect sugar in beets by NIR and mid-IR spectroscopies.

Mid-IR spectroscopy has also been used to determine the geographical and botanical origins of honey. Tewari and Irudayaraj[90] analyzed and correctly classified 350 honey samples from seven different floral sources. In a similar work, Ruoff *et al.*[85] have shown that mid-IR spectroscopy using an ATR cell can be very useful for the authentication of the botanical origin and also for the geographical origin; they have analyzed 11 unifloral and 411 polyfloral honey samples and used PCA and LDA to classify samples. Studies have also demonstrated that mid-IR spectroscopy permits one to determine the chemical composition and physical properties of honey.[91] For this, PLS regression models have been developed on the basis of collected spectra and reference values for major contents. The validation of the model exhibited R^2 values ranging from 0.81 to 0.99 with a repeatability ranging from 0.84 to 0.99.

Paradkar and Irudayaraj[92] have investigated the potential of FT-Raman spectroscopy to discriminate the floral origins (clover, orange, and buckwheat) of honey and to detect the presence of adulterants such as cane or beet invert sugar. Spectra collected have been interpreted, and chemometric models based on PLS and polymerase chain reaction (PCR) have been successfully established in order to predict adulterant content in honey from the three studied origins. Other studies concerning the determination by FT-Raman spectroscopy of sugar in honey have been undertaken.[93–95] Bands within the $1700-700\,cm^{-1}$ or $1800-500\,cm^{-1}$ range were selected to determine the contents of fructose and glucose.[93] Chemometric models have been built to determine the sugar content[95] and to differentiate honey according to its botanical origin.[94] A similar study has been realized by Arvanitoyannis *et al.*,[96] who applied multivariate analysis to group and detect honey samples of various origins.

Within the framework of the TRACE project, NIR and Raman spectroscopies have been deployed to develop models for honey from a specific PDO region. Three hundred and seventy three honey samples (219 Corsican and 154 non-Corsican, from France, Italy, Austria, Ireland, and Germany) were collected over a two-harvest period. The goal was to create a specific spectral fingerprint for Corsican honey. The best PLS-DA models developed using NIRS gave correct classification results of 90.0% and 90.3% for the Corsican and non-Corsican honey samples, respectively.[97] With models based on Raman data, 85.5% and 94.6% of the Corsican samples and the non-Corsican samples, respectively, were correctly classified as such. A similar study carried out by Hennessy *et al.*[98] on 150 honey samples from Europe and South America gave an overall correct classification of 93.3% and 94.7% using PLS-DA and FDA, respectively, on NIRS data. These results showed that NIR or Raman spectroscopy might be a suitable and alternative technology that could be easily implemented by both the industry and retailers to classify samples according their origin, with little sample preparation required and giving rapid results.

2.5 Authentication of kernels

Traceability also means being able to authenticate varieties or a class of varieties at any step of the food chain. The variety claim is the basis for quality control and the segregation of varieties dedicated for food industrial processing or feed. In order to identify and discriminate varieties, a large number of analytical methods have been developed, including visual examination of

the kernel morphology (color, size, shape, and texture); simple laboratory tests and measures (yield, thousand kernel weight (TKW), specific weight, kernel size, and germination analyses); and more elaborate and slower methods such as protein detection or DNA detection using the PCR technique for variety fingerprinting. Several studies have also shown the potential of NIRS for this purpose.

Studies reported on the use of NIRS for wheat analysis have firstly been concerned with the discrimination between wheat varieties on the basis of their bread-baking quality[99–102] and their hardness.[100] NIRS coupled to FDA has also permitted the correct classification (97%) of different commercial white flours,[103] but identification was mostly due to particle size and inorganic additives. In a similar approach, Cocchi *et al.*[104] tried to use NIRS to discriminate four commercial Italian bread wheat flours, but SIMCA results showed that not all groups could be classified; this was in contrast to the successful differentiation of Basmati rice samples from non-Basmati samples on the basis of NIR spectra of bulk samples.[105]

To meet the product quality specifications required by the world grain markets and the agro-food industries, NIRS analytical methods have been adapted for analysis at the kernel level. Kwon *et al.*[106] showed that an image-processing technique using a charge-coupled device (CCD) camera combined with an NIR spectrometer equipped with an optical probe enabled them to find some tendencies for varieties' identification. Williams *et al.*[107,108] showed that NIR hyperspectral imaging allowed for the correct classification of different types of endosperm in whole maize kernels according to the hardness that determines end-use processing performance. NIR hyperspectral imaging has also been used to characterize different origins of fonio (cultivated grains of *Digitaria exilis)* in order to study possible improvements in the productivity of this traditional cereal. The three classes (Bareng, Kankan, and Cinzana) studied were easily discriminated using PLS-DA, with more than 90% correct classification. A variety discrimination study of barley samples from multilocation and multiannual trials for barley registration in the Belgium catalog has also been performed by the CRA-W research team. A set of 1080 spectra acquired with a hyperspectral NIR-camera (10 kernels × 6 varieties × 6 locations × 3 years) was constructed. PLS-DA models gave 71–89% correct classification in prediction. Within the framework of the CO-EXTRA project,[12] we investigated the potential of NIR hyperspectral imaging, together with chemometrics, for the detection of genetically modified organisms (GMOs). Soybean and barley samples from various origins, some of them transgenic, were analyzed for this purpose. In all data sets, the results showed that good discrimination could be achieved in terms of the variety and presence of GMOs. NIR reflection spectroscopy has been used to discriminate European wheat varieties. The best model, based on a total of 249 samples from the 2003–2004 harvest, gave a correct classification of 94% for the validation sample set, including 12 wheat varieties.[109]

Hashimoto *et al.*[110] developed a mid-IR spectroscopic evaluation method using an FT-IR spectrometer equipped with an ATR accessory, for brewed coffee, the quality and taste of which depend greatly on properties such as geographical origin. They showed that some wavenumbers are specific for the discrimination between spectra of brewed Arabica and Robusta coffees. They also showed that brewed coffee from Brazil had different spectral features from those of the other studied Arabica coffees. Mid-IR spectroscopy has also been employed to discriminate wheat, oats, and buckwheat subjected to different technological treatments.[111] Results were encouraging in view of the prediction of the performances of flour matrixes in dough- and bread-making processes.

2.6 Authenticity of food/feed ingredients

Another aspect of establishing authenticity is to confirm, at various processing steps, the presence of specific ingredients claimed to be in a food/feed product, and also to detect possible contaminants (i.e., ingredients not claimed to be in a food/feed

product). Here, as well, vibrational spectroscopy can be of assistance to the food/feed sector.

With the emergence of the BSE (bovine spongiform encephalopathy) crisis, first in Europe in 1986 and later in other parts of the world, regulatory authorities have taken many legal decisions in order to ensure human safety. One of them was the total ban of the use of animal protein in compound feed. In order to control this ban, classical microscopy is the technique used as reference method in the EU; however, in the last few years, alternative methods such as near-infrared microscopy (NIRM) and NIR hyperspectral imaging have been studied for the authentication of feed ingredients and therefore the detection of meat and bone meal (MBM). Piraux *et al.*[112] published the first study in 1999, demonstrating the potential of NIRM for MBM detection in feedstuffs. With the NIRM instrument, a microscope is used to focus the IR beam on each particle of a sample spread on a sample holder, and its NIR spectrum is collected. The result of the sample analysis is the successive collection of hundreds of spectra, each one being the molecular NIR signature of a particle from one of the ingredients in the compound feed. The ingredients are identified using the spectral features measured over the wavelength range of 1100 to 2500 nm. Gizzi *et al.*[113] have described in their review, published in 2003, of the different methods for the detection of animal tissues in feed, the advantages of the NIRM method but also its weaknesses, especially concerning the limit of detection (LOD), which was equal to 0.1%; however, a few years later the LOD became as low as 0.05% mass fraction in the study of the dense sediment fraction obtained according to the procedure described in the EU microscopic guideline.[114] An NIRM method has been proposed to detect and identify, at species level, animal by-products included in compound feeds.[115] Treatment of spectra by SVM permitted the discrimination of fish meal from meal of other animal species with a 95 rate % of success.

In order to reduce the economic impact of a total ban of the use of MBM, analytical methods for detecting the presence of species-specific animal proteins in animal feed have been developed. With regard to the NIRS technique, species differentiation involves the development of a database and calibration equations at the species level. The NIRS methods can discriminate the higher taxonomic groups of species (terrestrial animal vs fish), and NIRS could have a role to play only as a screening technique.[116] Therefore, for species differentiation, research has focused on the NIR microscopic technology. The results achieved in the STRATFEED project indicate that the NIRM method is efficient for the specific detection of animal meal, and for discriminating between fish meal, mammal (pigs and cattle) meal, and poultry meal.[117] A limitation of this technique is the time involved in sequential collection of the spectra (particle by particle), but this has been solved by the introduction of the NIR hyperspectral imaging technology. This technology takes pictures sequentially of a predefined sample area at different wavelengths (*see* **Sampling Techniques and Fiber-optic Probes**). s8936 A complete methodology based on NIR hyperspectral imaging has been developed to detect animal ingredient particles in compound feeds.[118] The NIR imaging system allows for analyzing about 400 particles (76 800 spectra) in 5 min. NIR imaging spectroscopy has also been applied to the complete screening of feedstuffs in order to detect and quantify all feed ingredients included in a compound feed.[119,120]

Within the framework of a Belgian research project,[121] the NIR imaging method has been shown to yield very promising results when combined with SVM as a classification algorithm. The technique gives a detection limit of about 0.1% (depending on the number of analyzed particles), allowing a differentiation between fish and terrestrial animal sources.[122] In the SAFEED-PAP project,[13] NIRM and NIR hyperspectral imaging were studied for the species-specific quantitative identification of animal particles. The first NIRS models built on relevant NIR discriminant bands (NIR markers) led to an improvement in the specificity potential of the NIRS method for discriminating the source of animal particles.

With regard to contaminants, several projects have been funded by the EU for the development

of analytical methods to detect contaminants in food and feed. The results of the STRATFEED project[123] indicated that NIRS could provide the feed industry with a fast screening method for detecting the contamination of compound feed with animal by-products with an LOD equal to 1% at best[124] Among the objectives of the Cost Action FEEDFORHEALTH (2008–2011) project[125] are the evaluation of existing analytical methods, and the development and validation of new analytical approaches (including screening and rapid methods) for tracing the presence of undesirable substances. One of the tasks of the EU CON*ff*IDENCE project (2008–2012)[14] is to detect ergot in cereals using NIR imaging technology. The potential of vibrational spectroscopic techniques for tracing contaminants is promising within these challenges.

3 TRACEABILITY TOOLS

Consumer opinions collected within the framework of the TRACE project show that there is a demand for better dissemination of food traceability results and for more information on production methods, origin of the food, etc. There is also a real demand for a consumer-friendly and global labeling system. Simultaneously, there are questions about what the appropriate data for food chain traceability are and how they should be used by industry, authorities, and end-users. All the results that are shown through the examples in this chapter are issues from the scientific domain. One important challenge is how to interpret and translate the analytical results into specifications useful (and comprehensible) for the food processor and the consumer. There is a real need for creating a link between research and science communication. Rarely does the scientist have both skills, and communication is very often his/her last priority. Even if 60% of EU citizens agree with the statement that "scientists put too little effort into informing the public about their work," 52% think that the best qualified people to explain the impact of science and technology on society are scientists working in the public sector (universities and governmental institutions).[126] In this chapter, we provided an overview of some applications developed within the framework of EC projects dealing with traceability and authentication problems to deliver results using vibrational spectroscopic methods. The difficulty with regard to the spectroscopic analytical methods arises from the multivariate nature of measurements (or obtained fingerprints). The fingerprint of a sample collected at any point in the distribution chain has to be compared with that of typical samples or with that of the sample at one particular processing step. One solution might be a web address on a pack label. The website could contain the classification equation, which allows the user to predict an unknown spectrum collected by, for example, the food processor according to the type of material or the batch of material. The result could take the form of a "traffic light system" or a statement. One example of an on-line prediction tool dedicated to the laboratories is the RINA® (remote Internet NIR analysis) system, which enables each client laboratory to send its spectra over an Internet connection and get back the values estimated by predictive models stored on a dedicated server.[127] An example of tools dedicated to the consumer is the one proposed by Terra Creta S.A., which uses a "Traceability tree" tool. This tool allows the consumer to obtain via the web, from the batch number printed on the bottle, all the information needed about the product, at each stage of production, processing, and packaging.[128]

In this section, two other possible tools, developed within the framework of the TRACE project, are presented: the integrated chemometric toolbox for food authentication and the webmap interface for fingerprint models based on food origin.

3.1 The integrated chemometric toolbox for food authentication

The integrated chemometric toolbox (ChemTRACE) consists of fully tested state-of-the-art chemometric techniques for analyzing data obtained during food origin verification studies. It has been fully developed in MATLAB® and

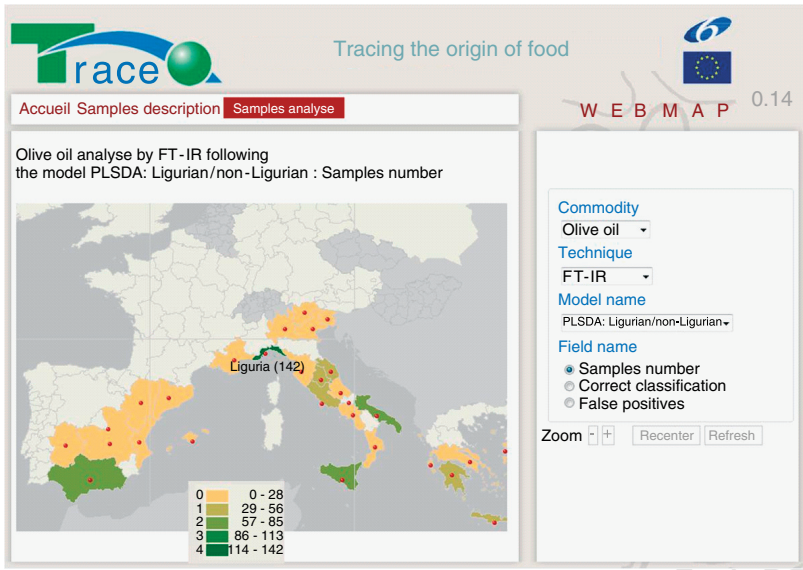


Figure 5. Webmap tool displaying olive oil samples collected by region and taken into account when developing a PLS-DA model (Ligurian vs non-Ligurian) based on the mid-IR spectra.

contains modules for robust PCA, robust SIMCA, classification and regression trees (CART), ANN, PLS-DA, and SVM. It also includes algorithms for data display and identification of outliers, as well as techniques dealing with missing values, splitting data, and predicting new samples. The performance of the modules has been tested and demonstrated with several data sets. The main achievement is that the toolbox has been developed into a tailor-made tangible product available to anyone involved in food verification studies.[129]

3.2 A webmap interface for fingerprint models based on food origin

The webmap tool is dedicated to disseminating, in a didactic way based on a webmap interface, the results from different fingerprinting and profiling methods. This webmap allows the display, on a map, of the description of samples according to their origin and of the classification results achieved with regard to the food commodity, technique, and model used. Each model used is defined and described in an attached file derived from an internal report or publication. The user can display on the map, for each region, the number of samples used to construct the model and the percentage of correct classifications and false positives for each group. Figure 5 shows a screen capture of olive oil samples collected by region and taken into account in the development of a PLS-DA model (Ligurian vs non-Ligurian olive oil) based on their mid-IR spectra.

4 CONCLUSION

The examples presented in this chapter have shown the high potential of vibrational spectroscopic methods in traceability to authenticate the geographical origin, the variety/species origin, and the production process of food and feed products through the measurement of organic compounds. The speed and the nondestructive aspects of the techniques, combined with the power of the chemometric tools, can help the producers, control laboratories, and authorities to trace the origin of the products according to their label and to authenticate the labeled ingredients. The monitoring of changes in product stability or identity as a result of production processes

or technologies used during manufacture is a big problem in the industry, but this problem is only partly addressed in this chapter. In order to solve the problem, new technological developments in NIR spectroscopy, using microelectromechanical system (MEMS) technology, for example, are being created. This can help in the application of NIR spectroscopic and chemometric methods in industry or in the field. MEMS technology is the integration of mechanical elements, sensors, actuators, and electronics on a common silicon substrate through microfabrication technology. As a breakthrough technology, many new MEMS applications are emerging, including spectroscopy, because of the increasing need for online analysis. Hand-held and miniature instruments are also increasingly required in the food and feed industry.

ABBREVIATIONS AND ACRONYMS

ANN	Artificial Neural Network
AOC	Appellation D'origine Contrôlée
ATR	Attenuated Total Reflection
BSE	Bovine Spongiform Encephalopathy
CART	Classification and Regression Trees
CCD	Charge-Coupled Device
DOC	Denominazione di Origine Controllata
DO	Denominación de Origen
EC	European Commission
EU	European Union
FDA	Factorial Discriminant Analysis
FT-IR	Fourier Transform Infrared
FT-NIRS	Fourier Transform Near-Infrared Spectroscopy
GMOs	Genetically Modified Organisms
LDA	Linear Discriminant Analysis
LOD	Limit Of Detection
MBM	Meat and Bone Meal
MEMS	Microelectromechanical System
Mid-IR	Mid-Infrared
MRE	Meal, Ready-to-Eat
NIR	Near-infrared
NIRM	Near-Infrared Microscopy
NIRS	Near-Infrared Spectroscopy
PCR	Polymerase Chain Reaction
PDO	Protected Designation of Origin
PGI	Protected Geographical Indication
PLS-DA	Partial Least Squares Discriminant Analysis
PV	Peroxide Value
SIMCA	Soft Independent Modeling of Class Analogy
SLDA	Stepwise Linear Discriminant Analysis
SPE	Solid-Phase-Extraction
SVM	Support Vector Machines
TKW	Thousand Kernel Weight
TSG	Traditional Speciality Guaranteed

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Abstract: Various labels preserve quality food products coming from particular geographical areas and protect consumers against imitations and false information. Traceability is an essential tool to enhance trader and consumer confidence in the safety, quality, and authenticity of the food. It also helps the regulatory authorities to detect fraud and dangerous substances. Traceability with regard to authenticity issues can be interpreted as verifying the labels, tracing the origin of food, or confirming the presence of ingredients claimed to be in that food. Scientific research in this area is focused mainly on developing analytical methods to authenticate the geographical origin of food, and also to monitor possible changes in food properties during storage, distribution, and up to the point of retail sale (i.e., degradation and aging over time). The use of vibrational spectroscopy (near-infrared, mid-infrared, and Raman) in traceability helps in authenticating the geographical origin, the variety/species origin, and the production process of food and feed products. In this chapter, several examples are discussed to illustrate the high potential of vibrational spectroscopy to tackle authenticity challenges. Some applications are also presented to interpret and translate the analytical results into specifications useful for the food processor and the consumer.

Keywords: vibrational spectroscopy, infrared, Raman, traceability, authenticity, food, feed, fingerprinting

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