Portable Vibrational Spectroscopy for Food Safety and Adulteration Screening

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Abstract

In this review we discuss various applications of portable vibrational spectroscopy in food adulteration analyses and confirmation of authenticity. These applications generally involve the adulteration of a food product with materials which may be of lesser monetary value and may also be detrimental to human health. Portable spectroscopic testing for food authentication opens potential for rapid and on-site analyses of food products at various stages in the food production chain. These portable techniques require the development of data analysis methods for each individual application, which will also be discussed in this review. Specific food safety applications for portable spectroscopy to be discussed include adulteration detection and evaluation of authenticity. Adulteration detection examples focus on the commonly adulterated milk powder and spice commodities, as well as the potential for component substitution (e.g., artificial sweeteners). For authentication, examples from marine oil dietary supplements, olive oils, honeys, coffees, and grains are presented along with examples of speciation (fish) and growth conditions (bell peppers). While a brief overview of the field, these examples show the utility of portable spectroscopic tools and chemometric modeling for regulatory applications.

1. Introduction

In this special issue for the *Journal of Regulatory Science* focusing on portable and emerging tools for food safety, vibrational spectroscopic methods can be highlighted. In fact, many thorough review articles have been published which highlight the value of portable vibrational spectroscopy-based methods to ensure the safety and authenticity of food products [39,40,44,52]. This portable, miniaturized analytical technology, combined with appropriate data analysis methods, has been successfully used for the detection of a wide variety of contaminants and adulterants, or the lack-thereof, in various food types. Portable spectroscopic devices hold promise for on-site, rapid, and low-cost detection, opening potential for adulterant identification throughout the food production chain.

In this review article, we discuss several applications of portable spectroscopy in food safety and authentication. Our focus in this limited-scope review is on those

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commodities that are more frequent targets for adulteration [43] and that lend themselves to successful analysis with vibrational spectroscopy and it's suitability for regulatory applications. For product authentication and verification (e.g., species, quality), portable spectroscopy can be used to ensure that the product composition is consistent with the information provided on the label. Closely linked to product authentication is economically motivated adulteration which is one of the oldest forms of fraud and occurs when there is a deliberate action to alter the food and then deceive the product's purchaser for economic gain. There are many forms of economically motivated adulteration including addition, concealment of damage or inferiority, substitution, and omission. Economically motivated adulteration is not just an economic issue. In some cases, the adulterants are detrimental to human health. Product authentication may involve analyses for multiple attributes. For example, honey authentication may involve analyzing the product for ingredient substitution (e.g., with corn syrup) and verifying the declared honey type on the label (e.g., Manuka honey).

For detection, vibrational spectroscopy can rapidly detect abnormalities in a product or specific adulterants to protect consumers from substandard or hazardous products. In these cases, portable mid-infrared (MIR)/near-infrared (NIR) and/or portable Raman spectroscopies were used in conjunction with appropriate data analysis methodologies. The aim of this review article is to highlight these food safety applications, as opposed to providing an in-depth overview of the technology found in portable spectroscopic instrumentation. For those readers interested in more information regarding the underlying operating principles involved with portable spectroscopies and associated data analyses, the authors recommend several articles that focus on portable instrumentation [5,11,16,40,54] as well as the individual examples in this review. Specific food safety applications for portable spectroscopy to be discussed in this article include adulteration detection (milk powders, spices, artificial sweeteners) and determination of authenticity (marine oil dietary supplements, olive oils, honeys, coffees, grains, fish species, bell peppers).

2. Milk Powder Adulteration

Economically motivated adulteration of milk powders has been known to occur via the substitution of authentic product for or addition of lesser value and potentially harmful adulterants. Adulterant materials may be added to create the appearance of a superior product such as in the melamine contamination events. [32,37] This melamine adulterant and other nitrogen-rich compounds (e.g., urea, cyanuric acid, dicyandiamide) mimic analytical protein content and increase the apparent quality and value of the milk. Specifically, melamine substitution to falsely inflate protein content in milk powder resulted in the reported illness of 294,000 individuals and at least four fatalities of infants and young children in China. [15] In addition to melamine, there have also been reports of falsified milk powder content due to the addition of less valuable plant proteins including soybean and pea isolates. [36,38,59] These plant proteins can be used to adjust characteristics of milk powder such as viscosity, flavor, and nutrition. Saccharides such as starch, sucrose, and maltodextrin also represent potential adulterants, which can be added to adjust density and freezing point of milk. [13]
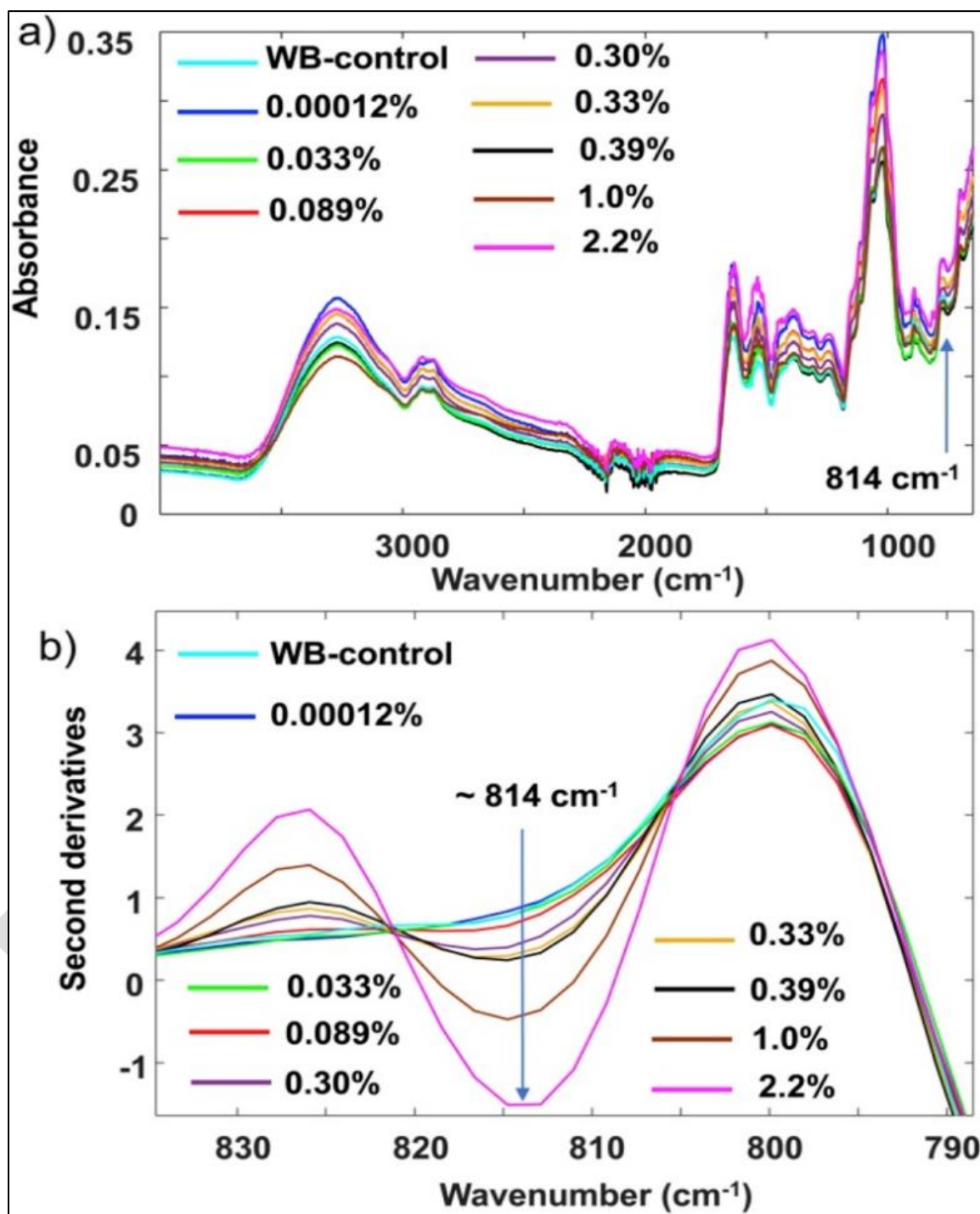
Figure 1. (a) ATR-FTIR absorption spectra of milk powder spiked with the adulterant melamine at various weight percent concentrations where WB-control is a wet-blended milk powder with no melamine, and (b) the second derivative + standard normal variate preprocessing spectra for the same samples. The band at 814 cm^-1 was associated with the melamine adulterant in the milk powder. Reproduced with permission from [34]

In analyzing the above-mentioned adulterants, detection may occur via either targeted or non-targeted chemical analysis.

Non-targeted, spectroscopic analysis is desirable in this circumstance, as it confirms the authenticity of the milk powder in a relatively simple and rapid manner, as well as potentially eliminating concerns regarding the introduction of novel adulterants into the milk powder. Portable NIR, MIR, and Raman spectroscopic methodologies have been used for this purpose, providing identification of adulterated or atypical milk powder samples. [32,34] Here, the presence of an adulterant or substandard product alters the spectroscopic signature of the milk powder which, in conjunction with chemometric modelling of acquired spectra, results in the detection of the atypical sample.

Limm et al. used portable Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) combined with Soft Independent Modelling of Class Analogies (SIMCA) chemometric modelling for the detection of adulterated milk powder. [34] Figure 1 demonstrates the portable ATR-FTIR spectra of a control un-adulterated milk powder sample, and a milk powder spiked with varying concentrations of the melamine adulterant. A peak at 814 cm^{-1} was attributed to the out-of-plane bending modes of the triazine ring of the melamine molecule, showing that melamine can be detected in milk powder down to concentrations as low as 0.089%. A Principal Component Analysis (PCA) model was then constructed which was used in combination with SIMCA for milk powder sample analysis. A 100% classification rate was reported for all samples above 1.0% melamine concentration in milk powder, and control (authentic) samples were successfully identified with a 97% classification. [34] This

study demonstrates the potential of portable ATR-FTIR in combination with chemometrics as a rapid analytical tool for the determination of milk powder authentication throughout the food production chain.

3. Spice Adulteration

Spices are known to be susceptible to economically motivated adulteration. [2,21,41,47,56] The high level of adulteration is due to various factors including high value for many spices as well as chopped or ground forms increasing susceptibility for adding in and hiding adulterants. Specifically, adulteration of spices may include dilution, substitution, and mislabeling. [21] Further, these adulterated spices may make their way through the food chain into processed foods without detection.

Potato starch, acacia, and annatto are potential paprika adulterants due to their low monetary value. [47] Oliveira et al. demonstrated the successful use of portable NIR for the rapid detection of paprika adulteration. [47] Here, paprika samples were spiked with potential adulterants over a range of concentrations, with a total of 315 mixtures used in the study. Following the acquisition of NIR spectra, partial least squares discriminant analysis (PLS-DA) chemometric modelling was performed to classify the samples as either adulterated or not adulterated. Good analytical figures-of-merit, including a specificity greater than 90% in prediction of the sample class and an error rate lower than 2%, were reported for the constructed PLS-DA models.

In addition to paprika adulteration, portable NIR has been applied to the authentication of other spices including turmeric and oregano.

Briefly, one known adulterant of turmeric is the relatively cheap dye metanil yellow, which mimics the natural yellow color of turmeric. [28,56] Portable NIR in combination with PCA and SIMCA chemometrics has been used to detect metanil addition in turmeric. [28,56] Here, NIR reflectance spectra were recorded for 248 pure turmeric, metanil yellow, and spiked samples (1-25% metanil yellow adulteration). PCA and partial least squares regression (PLS-R) models were developed, with the PLS-R modelling demonstrating superior predictive capabilities compared to the PCA methodology. In addition, portable NIR combined with PLS-DA and orthogonal-PLS-DA was successfully used for the detection of oregano adulterated with sumac, cistus, myrtle leaves, and olive leaves, with high prediction accuracies reported: 93% and 97% for authentic oregano and adulterated samples, respectively. [41]

4. Artificial Sweeteners

Artificial sweeteners, including saccharin and cyclamate, have been the subject of scrutiny for potential, and debated, health risks throughout the 20th century. [60,72] In addition, various countries around the world have differing regulations regarding these sweeteners. [7,60] Portable spectroscopy represents a rapid technique capable of aiding food suppliers and regulators in ensuring that artificial sweeteners are compliant with current regulations and are safe for human consumption. While several spectroscopic methodologies exist for artificial sweetener determinations [3,35,42], portable methodologies are less common.

One study in particular utilizes both portable NIR and portable Raman spectroscopy to detect artificial sweetener concentrations and substitution in tabletop formulations. [31] The portable Raman, portable NIR, and benchtop NIR spectra of the artificial sweeteners saccharin and cyclamate, along with spectra of associated fillers found in tabletop formulations, were first acquired. [31] Here, bands at 1594, 1176 and 697 cm^{-1} for saccharin and 1450, 1258, 1058, and 803 cm^{-1} for cyclamate in the portable Raman spectra were found to not overlap with other potential sample components (e.g., fillers). These characteristic spectral peaks were useful in the development of calibration models for saccharin and cyclamate quantitation. For the portable NIR analysis, a unique spectral feature was observed at 6033 cm^{-1} for saccharin and 4713 cm^{-1} for cyclamate in the second derivative spectrum, which ultimately led to an optimal portable NIR model. For both Raman and NIR PLS-R methodologies, specific spectral regions were selected which provided for models with reduced prediction errors, and calibration models were found to provide R^2 values >0.9. Results of this study showed predicted concentrations of saccharin and cyclamate in table-top sweetener formulations to be in good agreement, within 80-120% of the label declared sample concentrations. These results demonstrate the effectiveness of portable Raman and NIR spectroscopies in the determination of artificial sweeteners in table-top formulations, providing a rapid and portable analytical tool for both quality assurance and regulatory labeling verification efforts. [31]

In a separate study, portable Raman was successfully applied to the detection of counterfeit Stevia products, a natural sweetener. [65] Here, spectral matching with a 1064 nm Raman device was used for the analysis, without the use of chemometric analysis. Raman spectra of six commercial Stevia products were compared to those of artificial sweeteners including sodium saccharin and sodium cyclamate. Results showed a limit of detection of 5% w/w

sodium cyclamate in Stevia products. In addition, three out of the six commercial Stevia products tested were found to be counterfeit, thus highlighting the ability of Raman to detect adulteration and be used for product authentication. [65]
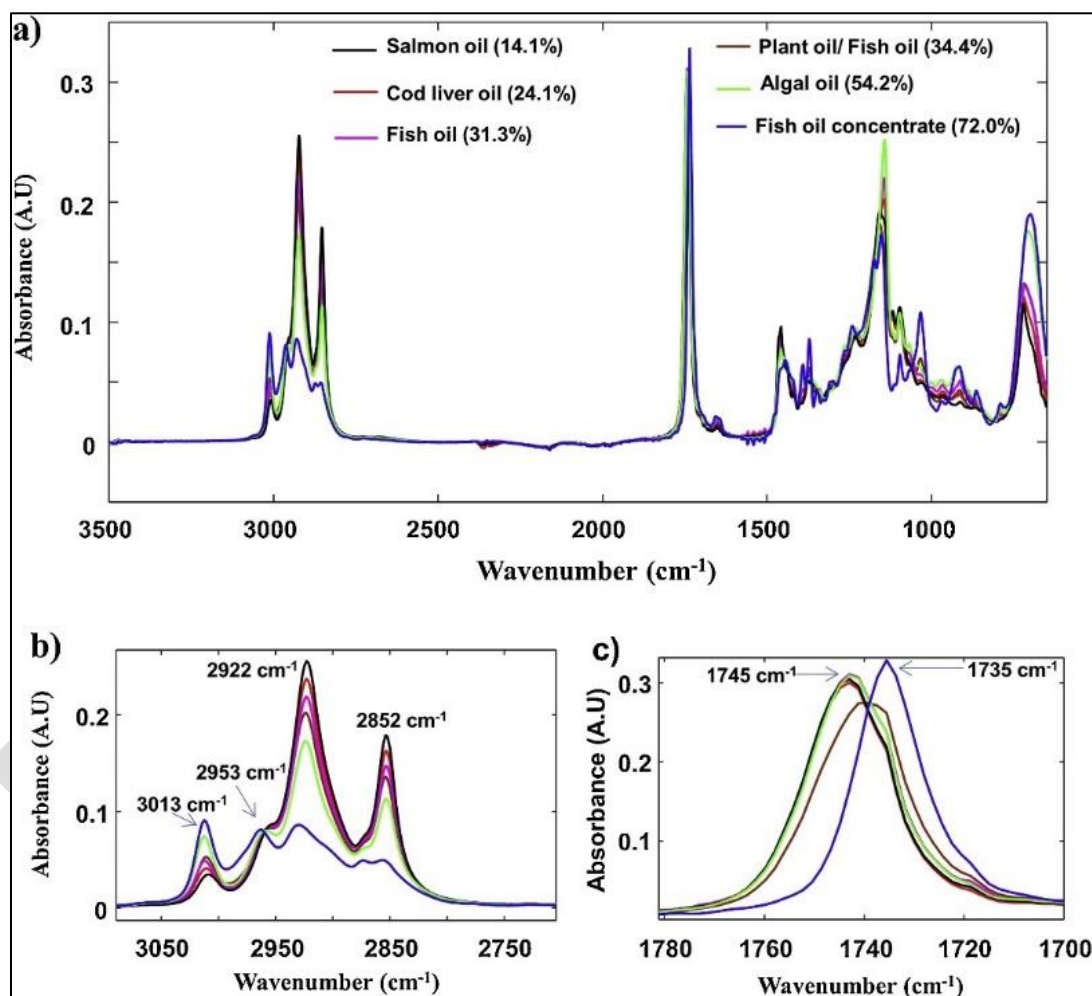
5. Marine Oil Authentication

Figure 2. (a) Portable ATR-FTIR spectra from six different marine oil product categories over the full wavenumber range of the portable device, and (b), (c) select ranges which were useful in the discrimination of various marine oil categories. Reproduced with permission from [29].

Marine oil dietary supplements contain omega-3 polyunsaturated fatty acids (PUFA) including docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA), reportedly with a wide range of potential health benefits. [27,58,62] These PUFAs may be present in both a triacylglyceride (TAG) form or an ethyl ester (EE) form, depending on the processing steps during manufacturing of the marine oil supplement. [29] The presence of either TAG or EE PUFAs is significant, as better bioavailability has been reported for

the TAG form. [1,45] The analysis of these fatty acids and their various forms is essential to ensuring the authenticity, product quality, and accuracy of label declarations of various marine oil supplements.

One study in particular uses portable ATR-FTIR spectroscopy for the classification of marine oil supplements into their TAG and EE components and for quantitation of EPA and DHA PUFAs. [29] Figure 2 demonstrates portable ATR-FTIR spectra of six different marine oil product categories. Spectral variation was observed which proved useful in subsequent PLS-DA and PLS-R chemometric analyses. Here, an ester carbonyl band at 1750-1730 cm^{-1} was associated with discrimination of the TAG and EE components. Ninety-five omega-3 PUFA products were used for building PLS-DA calibration models, leading to the correct classification of all samples into their TAG, EE, and mixed TAG+EE components. Further, developed PLS-R chemometric models from ATR-FTIR data showed good linear correlation with a reference Gas Chromatographic (GC) method ($R^2 > 0.91$) for DHA and EPA concentrations. [29]

In a separate study, PLS-R was compared to the use of support vector regression (SV-R) chemometrics for quantitative predictions of the concentrations of six different marine oil fatty acids, based on the portable ATR-FTIR marine oil spectra. [30] SV-R is a machine learning chemometric technique with a non-linear approach to calibration for quantitation, representing a potentially more accurate alternative to PLS-R for complex samples. Results showed SV-R to produce improved accuracies, up to 2.4 times higher, and improved prediction qualities when compared to the more commonly used PLS-R. In addition, the SV-R modelling was found to yield improved agreement with NIST-certified reference values for the prediction of EPA and DHA in three standard reference materials (SRMs). This improved accuracy is attributed to the ability of the SV-R to quantify non-linear relationships which exist in the marine oil spectra. [30]

In addition to ATR-IR, portable mid-IR spectroscopy combined with PCA and PLS-R has been used for the analysis of supplements with a wide range of EPA/DHA concentrations (0-60%) from various sources including fish oil, cod liver oil, and flaxseed oil. Here, PCA was used for classification of these oil sources based on EPA content, oil source, and oil processing factors. PLS-R models for quantitation of EPA and DHA demonstrated excellent predictive capabilities with high correlation coefficients, opening potential for rapid and robust screening of fatty acid compositions in marine oil supplements via portable mid-FT-IR spectroscopy. [51]

Portable Raman spectroscopy has also been applied to the analysis of marine oils, with three portable Raman instruments evaluated on a set of 104 marine oil products. [67] Here, PLS-R modelling was used to predict the fatty acid composition in each sample. Results showed success with yellow-colored marine oil supplements, although results were less satisfactory for red-colored samples. Overall, good agreement with GC-determined concentrations was demonstrated for the PLS-R calibration models, showing the potential of Raman spectroscopy in marine oil supplement determinations. [67] In a separate study, portable Raman spectroscopy was used for the quantitation of EPA and DHA omega-3 fatty acids in fish oil capsules. Here, 15 commercial samples were analyzed via handheld FT-Raman combined with PLS-R analysis, with results demonstrating good agreement with benchtop Raman spectroscopy determinations. [33]
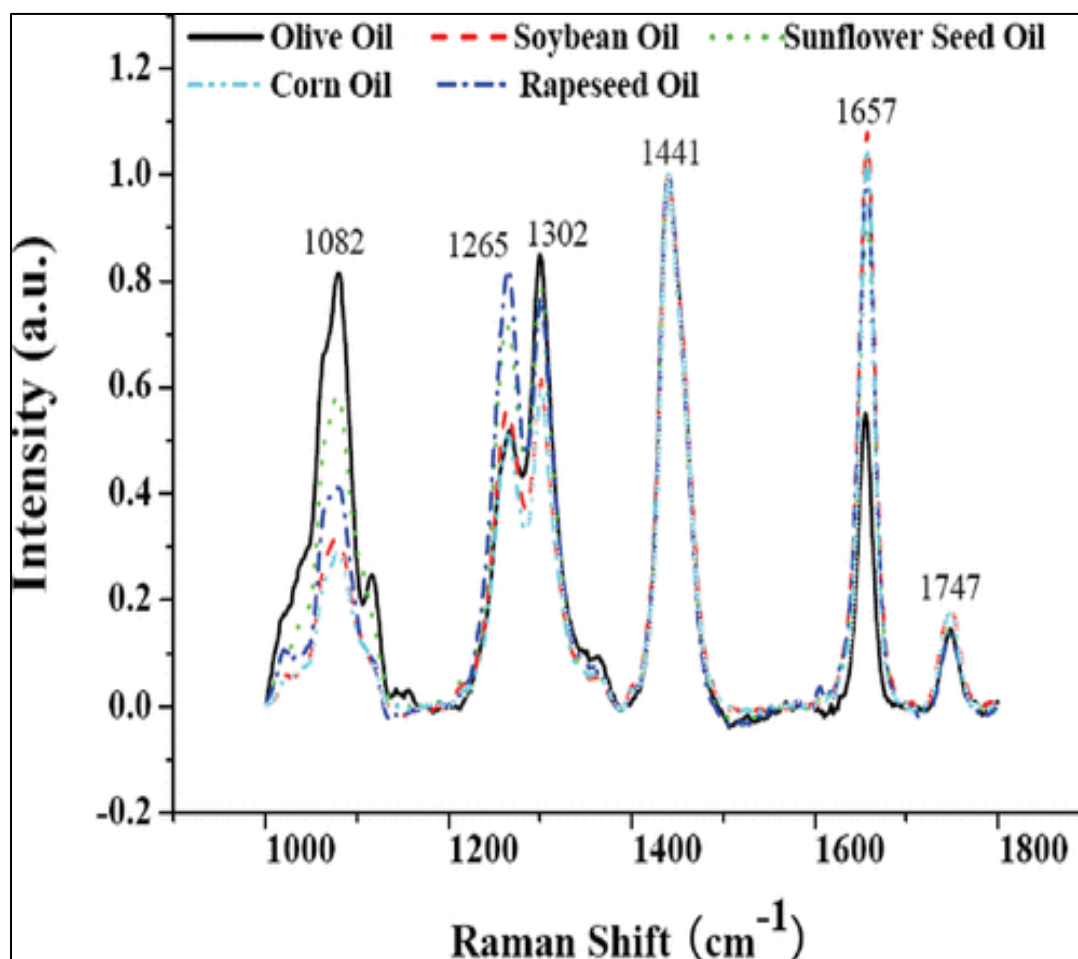
Figure 3: Raman spectra of olive oil and several potential olive oil adulterants including soybean oil, sunflower seed oil, rapeseed oil, and corn oil. Reproduced with permission from [71].

6. Olive Oil Authentication

The high commercial value of olive oil around the world has led to adulteration via the addition of low value oils such as soybean, corn, and rapeseed oil. [68,71]

The vulnerability of the extra virgin olive oil supply chain to food fraud has been studied, including the identification of various factors which may increase the susceptibility of olive oil to food fraud. [68] Portable spectroscopic detection of olive oil adulteration is important, as it increases accessibility of testing to on-site locations, without the need for high cost, time-consuming, laboratory-

based instrumentation such as Gas Chromatography-Mass Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC), and Nuclear Magnetic Resonance (NMR). Figure 3 shows portable Raman spectra of olive oil and several potential olive oil adulterants including soybean oil, sunflower seed oil, rapeseed oil, and corn oil. [71] Here, band intensities of the olive oil between 1800 and 1000 cm^{-1} were found to differ from the potential adulterants, serving as a basis for discrimination of the authentic product from the adulterants. Specifically, olive oil consists of mainly monounsaturated oleic acid, whereas soybean oil, sunflower seed oil,

rapeseed oil, and corn oil contain higher concentrations of linoleic acid. This difference results in intensity changes of bands at 1657 and 1265 cm^{-1} in the Raman spectra, which were used to discriminate the authentic from adulterated olive oil. These spectral peaks were then normalized by a peak at 1441 cm^{-1}, which showed a constant intensity across all of the oil samples tested. Finally, intensity ratios of 1657/1441 cm^{-1} and 1265/1441 cm^{-1} were plotted in a two-dimensional chart, providing for discrimination of the adulterants. Here, genuine olive oils were successfully discriminated from adulterated olive oils containing 5% or greater of added adulterant oils. This method presents a rapid and simple approach to the detection of adulterated olive oils, with no chemometric modelling necessary. [71]

In a separate study, portable NIR spectroscopy was used successfully to distinguish extra virgin olive oil from lower grades of olive oil including refined olive oil and pomace olive oil. [69] Here, SIMCA chemometric modelling was used for predicting the identity of the various oil grades. 130 olive oil samples were analyzed with results demonstrating the distinction of pure olive grades including extra virgin olive oil, refined olive oil, and pomace olive oil. [69]

7. Honey Authentication

Honey is reported as the third most adulterated food substance on the market. [49,70] This adulteration occurs via substitution with cheaper ingredients such as high fructose corn syrup and dextrose. [50] One study found adulteration in 27% of honey products tested, with these products originating from twelve different countries around the globe. [70] In 2013, large scale adulteration was found in a U.S. honey packing company, with the illegal purchase of honey from China. [25] In addition, in 2017 it was reported that 31% of honey in Canada was adulterated. [19]

In order to assess whether a honey product has been adulterated, non-targeted analysis is desirable, as any targeted analysis may fail to detect an unanticipated adulterant. Non-targeted, portable Raman spectroscopy combined with chemometrics is one technique that may be suitable for the authentication of honey samples. [4] This approach uses honey "fingerprinting" in combination with chemometrics to separate out any samples which fail to match an authenticated honey sample. Aykas et. al. subjected 97 honey samples to both portable and benchtop, 1064 nm Raman spectroscopy in combination with SIMCA modelling. [4] It is worth noting here that 1064 nm Raman was used in this study to successfully diminish interference from fluorescence, which can drown out spectral peaks from the sample when using shorter-wavelength Raman instruments. HPLC with Refractive Index (HPLC-RI) detection was used as a standard method for honey analysis to evaluate the performance of the Raman and chemometric methodology. Results of the portable Raman analysis with SIMCA demonstrated complete agreement with the HPLC-RI results, with 100% sensitivity and 100% specificity in classification of the honey samples as either authentic or adulterated.

In addition to Raman spectroscopy, successful honey authentication has been demonstrated in the literature via portable NIR with chemometric modeling. [18,23] In one study, honey originating from South Africa was successfully authenticated via NIR with PLS-DA chemometric modelling with high classification accuracies reported (e.g., >93%). [23]

8. Coffee Authentication

Another commodity where authentication is necessary to prevent lower quality via material substitution is coffee. For example, Arabica coffee possesses a high commercial value around the globe and is subject to potential adulteration via the addition of less valuable coffee varietals such as Robusta and other materials including corn, barley, and sticks. [10,17,53] These potential adulterants may be roasted to the same color level as the authentic Arabica coffee and covered in fine coffee powder, thus preventing the adulterants from being detected with the naked eye. [10] Various analytical techniques including benchtop spectroscopy, mass spectrometry, and NMR have been successfully applied to the discrimination of adulterated coffees from authentic ones. [9,14,17,48,55] However, very few are portable methodologies, thus presenting a limitation in the rapid and on-site analysis of coffee throughout the production chain.

Correia et al. used a portable microNIR device for successful determination of the authenticity or "quality" of arabica coffee via identification and quantitation of potential adulterants. [10] Following NIR spectral acquisition, data from 125 coffee blends composed of a mixture of authentic Arabica coffee and varying levels of adulterants were subject to PCA and PLS-R. PLS-R was successfully used for quantitation of various adulterants including corn and peels/sticks, with a limit of quantification in the range of 5-8 weight percent adulterant. [10] This study demonstrates a portable and rapid technique for the determination of authenticity of commercial Arabica coffee samples and may be applicable to other coffee species.

9. Grain Authentication

Rice is a common food staple around the globe and has large diversities in country of origin and high volumes being shipped throughout the world. Sophisticated and time-consuming laboratory-based analyses for the authentication of rice are insufficient for on-site analyses, opening potential for rice adulteration to go undetected. Rice may be adulterated through substitution of less valuable rice types. [63] Teye et al. have demonstrated the use of portable NIR spectroscopy for the authentication of rice from various geographic origins. [64] Here, 520 rice samples were analyzed, and the obtained handheld NIR spectra were used for PCA chemometric model building. Rice samples were classified by country of origin, quality grades, and imported versus local rice. Results indicated a greater than 90% correct classification rate for all categories of rice studied. [64]

The authentication of grains other than rice including quinoa, kañiwa, and kiwicha has been demonstrated using portable ATR-IR in combination with chemometric analysis. [61] Here, 106 samples were analyzed and subjected to SIMCA and PLS-R. Spectral differences arising from starch structure at 1100-900 cm^{-1} were reported to aid in the successful discrimination of authentic from adulterated grain samples. [61] This study opens potential for the rapid and on-site authentication of various grains throughout the food production process.

10. Fish Species Verification

The mislabeling of fish products and substitution of valuable fish species for cheaper species have been reported. [26,66] This may occur at various stages throughout the boat-to-table supply chain, including mislabeling during harvesting and fish substitution at the restaurant level. [46] Portable spectroscopy has been studied

previously for the speciation of fish and represents a rapid and non-destructive technique for authentication which can be performed at various points in the food production and marketing chains.

One study in particular uses handheld NIR with diffuse reflectance and an external laptop for the discrimination of two different species of mullet, two different species of cod, and two different species of trout. [46] Following spectral acquisition, PCA and SIMCA classification were used to separate the inferior species in the mullet, cod, and trout. This analysis represents rapid and portable methodology, which could be used by regulatory agencies for on-site authentication of various fish species from those of lower quality. [46]

A separate study evaluated the ability of portable NIR in combination with Linear Discriminant Analysis (LDA) and SIMCA to discriminate Atlantic cod versus haddock fish fillets and patties. [22] Results demonstrated the methodology to be reliable, with 100% correct classification reported for the LDA model. However, the authors noted that the LDA model may be misleading when the substituted fish species was not considered in the construction of the LDA model, and that SIMCA modelling may be more appropriate than LDA when determining if a fish species is authentic or fraudulent. [22] As these two studies highlight, fish speciation using portable spectroscopy is a promising area for future research.

11. Bell Pepper Verification

Portable spectroscopy has been used to assess the ripeness and quality of produce items such as fruit and vegetable. [6,8,12,20,24] While essential for food quality, these applications may not be readily applicable to economically-motivated adulteration and, as

such, will not be discussed here. However, discrimination of a vegetable based on the growing system used (e.g., outdoor vs indoor) may help to ensure food product authenticity and prevent food fraud via substitution of a food grown in an alternate food system perceived to be of less economic value.

In one example of authenticated growth conditions, Sanchez et al. demonstrated the use of portable NIR spectroscopy to distinguish outdoor grown bell peppers from those grown in a greenhouse. [57] Here, a portable NIR device was used in combination with both PCA and PLS-DA to separate bell pepper samples into outdoor and indoor grown classes. PCA demonstrated one NIR absorption peak useful in discriminating the peppers, and this peak was related to water content of the peppers due to the greenhouse-grown peppers containing lower dry matter content. Results of the study demonstrated 89.73% correct classification based on the growing system used with discrimination attributed mainly to differences in physio-chemical properties (e.g., water and sugar content) of the outdoor and indoor grown peppers. These results show the potential of portable NIR in the authentication of bell peppers based on the growing system, which may be carried out in a rapid and portable manner at any point in the food production chain from field to table. [57]

12. Conclusion

In summary, the use of portable spectroscopy for various common food authentication and adulteration applications has been demonstrated in this brief review on a number of food commodities. These techniques open the potential for rapid and on-site analyses of food products at various stages of the food production chain. These spectroscopic methodologies generally identify food

adulterants which are present in bulk concentrations as opposed to very low and trace levels (e.g., below 1%). Mid-IR, NIR and Raman spectroscopies are widely used portable spectroscopic techniques, each with their own advantages, and we refer the reader to excellent in-depth articles regarding these instrumentations. [11,54]. In general, these portable techniques require the development of data analysis methodologies for each individual application. However, once this application development is complete, the analysis may be conducted by non-experts with high ease-of-use. This represents a powerful tool in ensuring the authenticity and safety of food products around the globe, and an area of science which will transition into mainstream use in the years to come.

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