Chapter 5
Raman Spectroscopy

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1 Introduction

Raman spectroscopy is a non-invasive and non-destructive analytical technique that has established itself in the field of food industry for quality control, traceability and authenticity assessment. Raman spectroscopy rely on the inelastic scattering of monochromatic light by molecules which undergo vibrational transitions (Ferraro 2003). In a typical Raman experiment, a monochromatic laser light interrogates the sample, without or with minimum sample preparation, and the inelastic scattered light is detected to produce a Raman spectrum, representing the intensity of the scattered light as a function of the energy of the vibrational transition involved in the scattering process (Ferraro 2003). The Raman spectrum provides a molecular fingerprint of a molecule (specific position and relative intensities of the bands). Moreover, the intensity of the Raman signal is proportional to the number of scattering molecules in the sample (Banwell and McCash 1994). Thus, Raman spectroscopy gives information about the chemical composition and the molecular structure of the sample investigated. Actually, Raman spectroscopy is complementary to infrared spectroscopy (which is based on the absorption of light in the infrared range of frequencies), but offers several advantages compared to infrared spectroscopy, among which the ability to perform measurements in aqueous environment using visible light sources (Larkin 2018). For this reason, diverse and impactful

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applications of this non-destructive technique in the food industry have been developed enhancing consumer confidence, ensuring food quality and safety, and combating fraud and adulteration (Chen et al. 2023; Xiao et al. 2023; Petersen et al. 2021; Wang et al. 2021; Tena et al. 2019; Fernández Pierna et al. 2011; Yang and Ying 2011).

1.1 Origin of the Raman Bands

During a Raman experiment, the energy of the incident photons is shifted by discrete values that characterise the vibrational transitions happening in the sample at the molecular level (Ferraro 2003). These shifts can be understood by considering that the electric field associated with the incident radiation interacts with the electrons cloud around the molecules, thereby inducing periodic variations in polarization of the molecules (mostly from the ground vibrational level). As a result, the energy of the incident radiation is momentarily retained in the form of a molecular entity polarized (often called a virtual state). After a short retention time, the system returns either to its initial state (scattering exactly the same energy, in all directions, which is called the Rayleigh scattering) or to the first vibrational excited state. In the latter case, that occurs with a low probability (typically one Raman photon scattered for every 10^6 to 10^8 incident photons), the frequency of the light scattered will thus be lower than the frequency of the exciting light, by an amount of energy that corresponds to the energy difference between the fundamental state and the first excited state of vibrational energy. This is the Stokes contribution of the Raman effect (Fig. 5.1). Actually, the Raman scattering is a symmetrical effect relative to the laser line, for some molecules, initially in the first excited state of vibrational energy may relax to the ground state, scattering light whose energy is higher that the energy of the incident photons (Fig. 5.1). However, that contribution, called the anti-Stokes effect, is even less probable than the Stokes scattering, and is not often considered for analytical developments.

Raman spectra are composed of several bands, each of them corresponding to an active vibrational transition of one molecule (Larkin 2018). The position of the Raman band is expressed as the wavenumber shift (in cm^{-1}) with respect to the excitation laser line, and is known as the Raman shift. The laser line is by definition at a Raman shift of 0 cm^{-1}. The position of the bands depends on the atomic composition and on the strength of the vibrating molecular moieties (either a single bond or a few bonds whose vibrations are concerted). A Raman spectrum can therefore be used for identification purpose by locating the position of the different bands in the spectrum. Many tables with characteristics Raman shift for chemical functions can be found in the literature (Socrates 2004). It is important to remember that, as the band position is the energy required for the vibration transition, tables referencing the position of the vibration modes in infrared can be used to attribute vibration mode in a Raman spectrum.

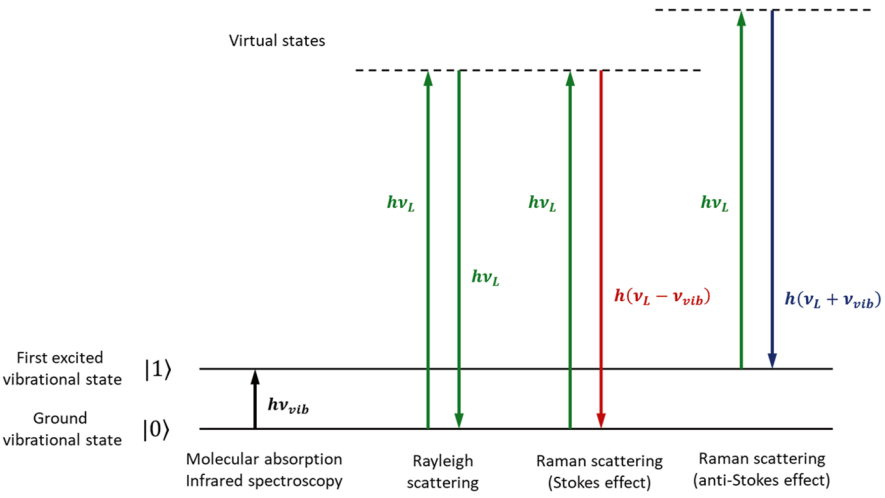

Fig. 5.1 Energy diagram illustrating the vibrational molecular absorption in the infrared (IR spectroscopy), the Rayleigh scattering (elastic scattering of the laser light with the frequency ν_L), and the Raman scattering (inelastic scattering) involving either a photon whose energy is decreased (frequency $\nu_L - \nu_{vib}$, Stokes effect) or increased (frequency $\nu_L + \nu_{vib}$, anti-Stokes effect) by an increment of energy associated with the vibrational transition ($h\nu_{vib}$)

In the context of food analysis, bands related to proteins content can generally be observed in the range of Raman shifts between 1645 and 1685 cm^{-1} (assigned to the C=O stretching, amide I mode) as well as between 1200 and 1350 cm^{-1} (amide III mode), where the vibration mode of amide bonds present in proteins can be observed. Other bands characteristics of specific amino-acid, such as the band related to phenylalanine around 1004 cm^{-1} (breathing mode of the phenyl group), also allow to evaluate the protein content. Raman spectroscopy can also be used to evaluate the content of lipid in food samples, by following the intensity of specific bands located around 1750 cm^{-1} (assigned to the C=O band in fatty acids), around 1660 cm^{-1} (related to C=C bonds in unsaturated lipids) or in the vicinity 1470–1440 cm^{-1} (related to CH_2 groups in the hydrocarbon chains). Bands characteristic of other general classes of molecules (carbohydrates, vitamins, etc) are also well documented (Socrates 2004).

2 Raman Instrumentation, Sample Preparation and Operating Parameters

2.1 Raman Instrumentation, a Brief Overview

The selection of an appropriate Raman instrument is essential in order run successful analyses of samples. Conventionally, two main types of Raman instruments are available on the market: the non-dispersive and the dispersive Raman instruments

(Smith and Dent 2019). In the former, NIR laser sources (typically Nd:YAG laser emitting at 1064 nm) are employed and the spectral discrimination of the scattered light is based on an interferometer. The spectrum is eventually retrieved after Fourier Transform of the recorded signal (interferogram) and these instruments are known as Fourier Transform Raman (FT-Raman) spectrometers. On the other hand, the dispersive spectrometers use various visible laser lines for Raman excitation and the detection system consists of a dispersive monochromator (e.g. either a reflection or transmission diffraction grating) which projects the dispersed Raman light onto a 2D silicon-based phototransducer arrays or grids that are known as charge-coupled device (CCD), or more recently complementary metal oxide semiconductor (CMOS) detectors. While in principle Raman scattering can be collected in every direction from the sample, the backscattering configuration (illustrated in Fig. 5.2) is the most common configuration of commercially available instruments, including the benchtop confocal micro-Raman spectrometers, or miniaturised portable and handheld spectrometers (Smith and Dent 2019). The best analytical performances are obtained with stable benchtop instruments installed in an adequate lab environment. Miniaturised instruments enable *in situ* analyses on the field, for instance directly on food stock (Beganović et al. 2019). However, the spectra produced with this kind of equipment are often characterised with a lower spectral resolution and sometime with a lower signal due to size and energy budget (especially if the

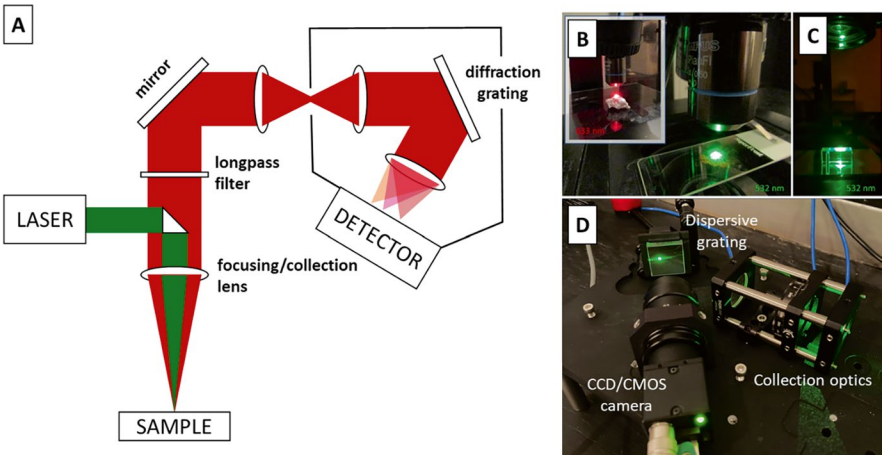

Fig. 5.2 Optical designs of a dispersive Raman instrument. (**a**) General design of a dispersive instrument with a 0° collection design where the focusing lens is also the collection lens. The incident beam is depicted in green and the collected light is depicted in red. Optical fibre probes can be used to bring the laser light to the sample and to carry the collected Raman light to the monochromator. Also, the monochromator can be replaced by an interferometer for instrument operating a NIR laser (i.e. 1064 nm). (**b**) A micro-Raman spectrometer operating with different laser sources through long-working distance refractive objectives of the microscope. (**c**) Close-up on a solid sample irradiated with the lens of a Raman probe coupled to a Raman spectrometer by optical fibres. (**d**) Collection optics and grating of a portable Raman spectrometer interfaced with a 532 nm laser

instrument is powered by batteries), as opposed to the situation with benchtop instruments (Smith and Dent 2019; Vandenabeele et al. 2014).

The evaluation of Raman signals is key for analytical applications: the energy, wavelength or wavenumber associated with the Raman signals enables the identification of constituents into a sample, while the determination of the signal intensities can be used for quantitative analysis of these compounds. Equation 5.1 gives the general relationship between the Raman intensity and the amount of molecular scatterers: where I is the intensity of a Raman band of interest, k_I is the overall spectrometer response coefficient, k_S is the overall sample response coefficient, and finally C is the concentration of the active molecule (Ferraro 2003). k_I depends on the instrument operating parameters such as the laser wavelength and its incident power, the transmission and collection optics and the detector response. k_S considers the effect of the medium self-absorption and the molar scattering coefficient of the vibration mode of interest on the detected signal.

$$\boldsymbol{I} = \left(\boldsymbol{k}_I\, \boldsymbol{k}_S\right)\boldsymbol{C} \tag{5.1}$$

2.2 Selecting the Right Laser Source

The selection of the laser wavelength (or frequency) is one of the critical operating parameters of Raman experiments. Indeed, the intensity of the Raman scattered light is proportional to the fourth power of the frequency of the incident light, according to the Rayleigh laws of scattering. Therefore, the shorter the excitation wavelengths, the stronger the intensity of the scattered light (McCreery 2001): the Raman scattering is about five times more efficient with a 532 nm irradiation than with a 785 nm irradiation. The use of shorter wavelength lasers is thus attractive to maximise the sensitivity of the analysis. However, these shorter wavelengths are capable to promote molecular electronic transitions that are more likely to cause fluorescence (Ferraro 2003).

Fluorescence can be caused by the molecule under investigation itself, but also by the food matrix or by potential contaminants in the sample. Fluorescence is a major interference for Raman spectroscopy, which often overwhelms the Raman spectra with a continuous and intense background signal. Therefore, even fluorescent compounds present in very low amount can completely hinder the Raman signal of the main food product. Modern Raman instruments are generally equipped with several laser spanning the visible range of wavelength, enabling to find a compromise between the highest Raman signal and lowest fluorescence background (Smith and Dent 2019). Indeed, as shown in Fig. 5.3, while the Raman signal is scattered at the wavelengths following the excitation laser, the fluorescence signal will remain emitted at the same wavelengths dictated by the electronic transitions possible in the sample, hence changing the laser source can help discerning both spectral contributions. The use of FT-Raman and 1064 nm excitation lasers can

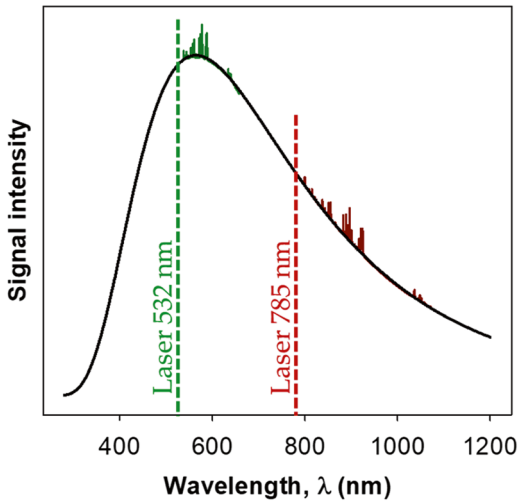

Fig. 5.3 Relative Raman signal observed with a 532 nm (green) or a 785 nm laser (red) on top of a fluorescence signal. These spectra illustrate that the molecular fluorescence is larger in wavelengths (typical half width at half maximum of a few hundreds of nanometres) than the Raman signals (typically the half width at half maximum is of a few nanometres)

ultimately be implemented when the sample is excessively fluorescent, even with longer laser wavelength (785 nm), but at the cost of a decreased sensitivity.

Besides the laser wavelength, the laser power applied to the sample is also an important operating parameter that has an influence on the Raman intensity measured. In general, the higher the laser power applied to the sample, the higher the Raman signal, assuming no phase transformation or thermal damage is caused to the sample (Ferraro 2003). The appropriate laser power is dependent on the wavelength of the laser selected (shorter wavelengths are intrinsically more energetic), on the focusing optics of the Raman instrument (the energy increases on the sample as the laser footprint or spot size decreases down to typically 1–2 μm^2 in the focalisation plan), on the properties of the samples (non-coloured samples will generally be less concerned with thermal degradation), and on the duration of the analysis. Therefore, the laser power on the sample should always be adapted depending on the nature of the sample.

2.3 Sample Preparation and Presentation

Raman spectroscopy is widely known for the minimum sample handling and preparation that is generally required (Smith and Dent 2019). Most of the time, bulk solid samples (e.g. blocks or films) can be directly placed in the laser beam path and a spectrum can be recorded by focalising the light at the surface of the sample. Solid powders can be deposited on inert support (e.g. glass, aluminium or stainless-steel slides) or held in containers exposing the top surface (often flattened) to the laser. Powder samples can be placed on rotating holders to increase the sampling area, hence reducing the influence of local heterogeneity. Liquids and gases can be placed

in transparent cuvettes or containers with transparent window (e.g. glass, quartz or sapphire). Non-volatile liquids can also be analysed in the form of drops deposited on inert solid surfaces. Thin and transparent samples (either solid or liquid) can also be placed on reflective surfaces to increase the signal intensity by reflection. Mirrors can be placed behind transparent cuvettes to also increase the signal for liquid analysis. Temperature-controlled sample holder can be mounted for samples requiring control of the temperature during analysis.

Spectrometers can be interfaced with fibre optic probes, microscopes, telescopes or other sampling accessories depending on the physical state, the quantity and the intrinsic heterogeneity of the samples (Vandenabeele 2013). Indeed, the instrument optics directly influences how the sample is illuminated and which volume of material is analysed. The incident laser power is delivered through the optics on the sample with a certain laser footprint (i.e. the surface of the sample that will receive photons from the laser beam), the laser power is therefore more often expressed as the power density or irradiance (i.e. laser power per surface unit). Yet, the number of excited molecules actually depends on the volume of materials irradiated by the focused laser beam. The volume of sample probed by the laser beam can be ideally (for isotropic and transparent samples) represented by a truncated hourglass timer shape for which the beam diameter d corresponds the spot size (laser footprint) when the beam is focused on the focal plane of the objective (Fig. 5.4). The depth of penetration (or depth of field), D, depends on the laser divergence and the numerical aperture (hence the focal length) of the focusing lens of the incident optics (Vandenabeele 2013). However, the effective sampling volume is ultimately dependent on the sample properties, such as the sample thickness, its possible grainy structure or its optical absorption property (McCreery 2001).

For example, coloured samples, either solid or liquid, may partially absorb the excitation and the scattered light, leading to a decrease of the Raman signal reaching the collection optics. Absorption of light will also lead to local increase of the temperature that may locally alter the chemical composition of the sample including phase transitions or thermal degradations, which in the worst-case lead to the burning of the sample. Finally, samples such as powders with grain size in the order of the magnitude of the laser wavelength, may diffuse the laser light, which lead to a larger volume of sample analysed compared to the situation of isotropic transparent samples (Fig. 5.4).

2.4 Spatial/Spectral Resolution

Spatial resolution achievable during Raman analysis is greatly dependant on the optical characteristics of the instrument used. Micro-Raman systems offer many advantages as they are designed to operate with multiple sets of objectives and also allow coupling to optical probes through optical fibres (Smith and Dent 2019). The high spatial resolution that can be achieved by these instruments (typically down to a few hundreds of nanometres, depending on the characteristics of the microscope,

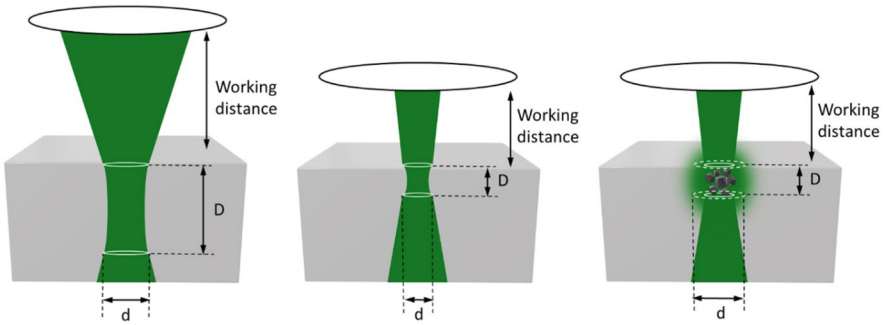

Fig. 5.4 Representation of the ideal profile of the laser, depicted by a cylinder with a thinner beam waist corresponding to the laser spot, d, when the beam is in the focal plane of the lens. The depth of field, D, also emphasis the volume of sample irradiated. Three situations are represented: lens with large working distance and depth of field probing an isotropic sample (left), lens with a small working distance and depth of field probing an isotropic sample (centre) and a lens with a small working distance and depth of field probing a sample made of particles smaller with size similar to the laser spot (right)

the objective numerical aperture and magnification, the wavelength of the laser fixing the diffraction limit) is a major benefit for Raman qualitative analyses of solid samples, such as geological or pharmaceutical materials, biological tissues, art and archaeological objects or food products (Vandenabeele 2013). If quantitative analyses are developed on heterogeneous solid samples (like food stock), however, it is preferable to use an optical system that has a larger Raman sampling capability, in order to have access to the composition associated with the bulk sample (homogenised). Typically, FT-Raman and portable dispersive instruments equipped with fibre-optic probes that use long-working distance lenses generate large laser footprints on samples, which facilitate the evaluation of bulk sample compositions.

The spectral resolution, defined as the wavenumber difference of two spectral lines still distinguishable, is dependent on many factors and high spectral resolution is not always mandatory for specific applications. The spectral resolution varies from 0.1 to 0.5 cm^{-1} for high resolution benchtop instruments to 10 cm^{-1} for portable instruments (Vandenabeele et al. 2014). In dispersive instruments, the spectral resolution is dictated by the resolving power of the diffraction gratings, the focal distance of the monochromator and the size of the pixels on the multichannel CCD/CMOS camera (Smith and Dent 2019). Several gratings are usually available on benchtop instruments, ranging typically from 300 grooves/mm (red excitations lasers) to 1800 grooves/mm (green and blue excitations lasers). Larger groove density will better separate light, enabling higher spectral resolution but reducing the range of wavenumber observable on the detector. Higher groove density (2400 grooves/mm or higher) are restricted to instruments with specialised focus on high resolution analysis or using UV excitation lasers. The monochromator focal length is also a highly important parameter: the longer the focal length, the higher the spectral resolution. This factor explains why the spectral resolution achievable on

benchtop instrument is usually much higher than on miniaturise portable instruments. Other parameters such as the detector pixel size, the laser wavelength and the slit entrance of the spectrometer also influence the spectral resolution. In FT-Raman, the spectral resolution is dictated by the oscillating distance of the mobile mirror in the interferometer: the longer the distance, the higher the spectral resolution (Vandenabeele 2013). Again, miniaturised portable instrument requires robust and small interferometers, hence are characterised with a lower spectral resolution than their benchtop counterpart that are larger and operate in stable lab environments (Vandenabeele et al. 2014).

3 Advanced Modalities of Conventional Raman Spectroscopy

The main limitation of Raman spectroscopy is its inherent lack of sensitivity, as only about 1 out of 10^9 of the incident photons will undergo inelastic scattering (Dietzek et al. 2010). Generally speaking, for bulk analysis the lowest concentrations that can be detected with Raman spectroscopy are in the range of 10^{-3} to 10^{-4} M. However, advanced modalities of Raman spectroscopy have been developed throughout the years with the principal goal of increasing the sensitivity of the technique. Advanced modalities used in the field of food analyses and monitoring will be briefly described here.

3.1 Resonant Raman Spectroscopy (RRS)

In typical Raman spectroscopy experiments, the wavelength of the incident laser is located in the visible or near-infrared (NIR) range. Therefore, for most organic molecules, the energy of the exciting laser is well below the energy required to induce an electronic transition in the molecule under investigation. Indeed, most organic molecules undergo electronic transitions only in the ultraviolet range of wavelength. However, for some organic molecules with particular chromophore groups, electronic transitions can be promoted by the absorption of photon in the visible or near-infrared range of wavelengths. When the excitation laser wavelength is close to the maximum of the electronic absorption band of the chromophore, the intensity of Raman bands of the chromophore group undergoes selective enhancement by a factor of 10^3 to 10^6 (Ferraro 2003). This resonant Raman spectroscopy is highly interesting because it strongly increases the sensitivity of the technique and is readily implemented with classical Raman instruments, without further modifying or processing the sample. However, this variation is only applicable to molecules with chromophore groups absorbing light in the visible to NIR range of wavelength. Typical examples of such molecules with relevance in food analysis are β-carotene

(absorbing light in the 360–600 nm range), chlorophyll (absorbing light around 400 and around 660 nm), or dyes added to provide colour to food, such as Sunset Yellow (absorbing around 480 nm) or Brilliant Blue (absorbing around 630 nm). In practice however, most molecules will more likely emit fluorescence than exhibit resonance Raman when laser light matching the energy of an electronic transition is used, making resonant Raman spectroscopy applicable in specific applications.

3.2 Surface-Enhanced Raman Spectroscopy (SERS)

Surface-Enhanced Raman Scattering (SERS) is a phenomenon where the Raman signal intensity of a molecule is increased when the molecule is located in the proximity of a nanostructured metallic surface (Fig. 5.5). SERS provides another way of increasing the sensitivity of Raman spectroscopy, but not restricted to molecules with resonance properties (Stiles et al. 2008). The SERS effect can lead to enhancement of the signal by factors as high as 10^{14}, even allowing single molecule measurements (Wang et al. 2020). However, for practical applications using classical nanosubstrates, the enhancement factor is usually in the range 10^5–10^7. Most SERS applications rely on the use of coinage metal (Au, Ag, Cu) for the nanosubstrate material. Nanostructures composed of these metals exhibit an essential property for SERS, which is localised surface plasmon resonance (LSPR) (Le Ru and Etchegoin 2009). Briefly, the enhancement of the Raman signal intensity in SERS finds its origin in the interaction between the incident laser and the LSPR of the nanosubstrate, giving rise to an increase of the electric field at the surface of the nanosubstrate and therefore enabling more intense Raman scattering from molecules located on the surface.

The wavelength of the LSPR of the nanosubstrate strongly depends on the nature, shape, size and spatial arrangement of the metal used as substrate (Wang et al. 2020). This high tunability allows SERS to be used with a wide variety of lasers, making it a highly versatile technique. As mentioned before, molecules need to be close (a few nm) to the surface to exhibit signal enhancement through SERS. This can be a limitation when molecules to be analysed do not exhibit a strong affinity

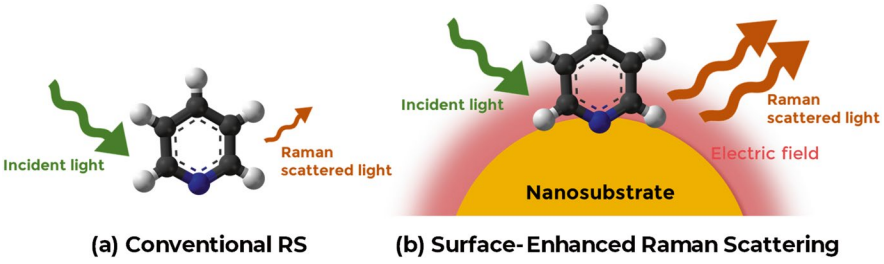

Fig. 5.5 Illustration of the conventional Raman scattering (**a**) and of the Surface-Enhanced Raman Scattering occurring at the surface of a nanosubstrate (**b**)

toward the surface of the substrate. SERS can also be combined with resonance Raman enhancement for suitable analytes, further increasing the detection sensitivity by performing Surface-Enhanced Resonance Raman Scattering (SERRS).

Nanosubstrate used in SERS are classified in two general categories: colloidal nanoparticles (NPs) or solid nanostructured substrates (Mosier-Boss 2017; Lin et al. 2023). Colloidal NPs can be either directly mixed with liquid matrices or dropped/sprayed on solid samples. For solid nanosubstrates, liquid samples can be directly dropped on its surface, and solid samples must generally be further processed before analysis. However, flexible and/or adhesive solid SERS nanosubstrate are increasingly being developed and can be used to extract analytes of interest directly from the surface of solid samples, such as fruits or vegetables, without damaging them (Lin et al. 2023). This kind of approach is mostly implemented for the detection of trace analytes likely to be found on the surface of the samples, such as pesticide residues.

3.3 Spatially-Offset Raman Spectroscopy (SORS)

Conventional Raman spectroscopy is limited in its ability to perform depth analysis of diffusely scattering samples (more commonly referred to as opaque or non-transparent samples). These include most food and biological samples, some plastic packaging or bottles, or even liquids such as milk. Analysis is therefore generally limited to the surface or near-surface for these materials (several tens or hundreds of microns depending on the optical setup and properties of the sample), making it challenging to perform non-invasive analysis of analytes contained inside or buried under such materials.

The limited number of photons that do originate from deep layers in the sample are often masked by Raman signals originating from or near the surface of the material. The basic principle of SORS is that the sample illumination and the scattered light collection are separated by a spatial offset (Mosca et al. 2021). This offset allows the rejection of surface scattered photons, making Raman analysis at larger depth possible (Mosca et al. 2021). Moreover, the magnitude of the offset can be tuned to control the probed depth within the sample (Fig. 5.6), making it possible to analyse successive layers, or to go through various thickness of packaging. Typical SORS experiments require at least two measurements, one with no spatial offset to obtain the spectrum of the surface layer, and one with a spatial offset from which the surface spectrum will be subtracted to isolate the spectral contribution of the subsurface material (Mosca et al. 2021). SORS is therefore a very attractive technique in food analysis thanks to its ability to perform through-package measurements.

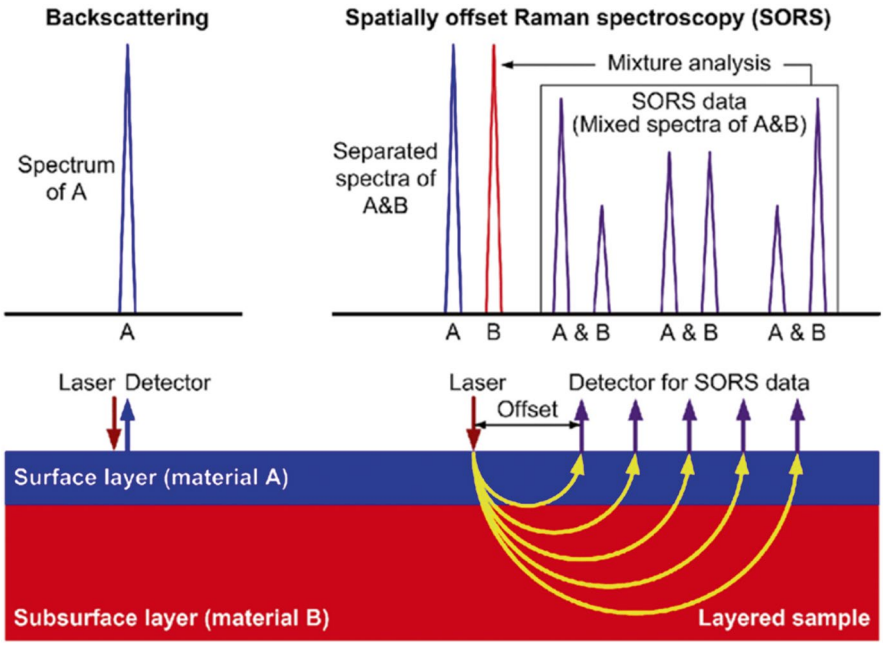

Fig. 5.6 Comparison between conventional backscattering RS measurements and SORS measurement. (Adapted from Qin et al. (2017) with permission from Elsevier (Copyright 2017))

4 Applications of Raman Spectroscopy in Food Integrity

The Raman technique has been and is being applied in different areas within the agro-food sector due to its many advantages. These advantages relate to the non-destructive nature of the measurements (it requires minimal sample preparation and does not damage or alter the food being analysed, making it ideal for routine analysis without compromising the integrity of the product); its high sensitivity and specificity, which allows even small levels of adulterants or contaminants to be identified; its cost-effectiveness (once the initial equipment is installed, Raman offers a cost-effective solution for continuous monitoring); its multiplexing capabilities (it allows simultaneous detection of multiple contaminants in a single analysis, making it efficient for comprehensive screening) and its capacity to perform real-time screening of products during production, distribution, and even at points of sale. This facilitates quick decision-making to prevent fraudulent products from entering the market or reaching consumers (Abbas et al. 2020; Vermeulen et al. 2017). The different areas of application of Raman in the agro-food sector can be grouped into two main categories: the application for quality control and its use for authenticity and traceability issues.

4.1 Raman for Quality Control

The use of Raman for quality control includes studies for a quick and accurate chemical composition analysis through the determination of components present in food, such as carbohydrates, proteins (Kuhar et al. 2021), fats (Esmonde-White et al. 2022), vitamins, and minerals (Zarei et al. 2023). It aids in monitoring nutritional content and ensuring compliance with regulatory standards (Herrero 2008). In this context, Raman has been also used for the characterization and discrimination of phenolic compounds, which are the most abundant secondary metabolites in plants (Baranska et al. 2004; Baranska et al. 2006; Pompeu et al. 2018), but also for other food products as cheese (Stocco et al. 2024) or salmon (Jensen et al. 2020), among others. Representative Raman spectra obtained for salmon can be seen in Fig. 5.7. Currently, the SORS technique is used for a wide range of food products, such as the assessment of the nutrient content of potato tubers, as well as for the identification of potato varieties (Morey et al. 2020) or the identification and extraction of information from subsurface shrimp meat (Liu et al. 2023). Raman is also an important method for the detection of contaminants. It is crucial to identify contaminants like pesticides, toxins, or heavy metals in food. Raman spectroscopy plays a crucial role in the detection and identification of various contaminants in food products by facilitating a rapid screening, enabling early detection and prevention of contaminated products from reaching consumers. Its high sensitivity and specificity make it a valuable tool for analysing and identifying contaminants. It ranges from pesticides (Zhai et al. 2016; Dhakal et al. 2014), toxins and mycotoxins

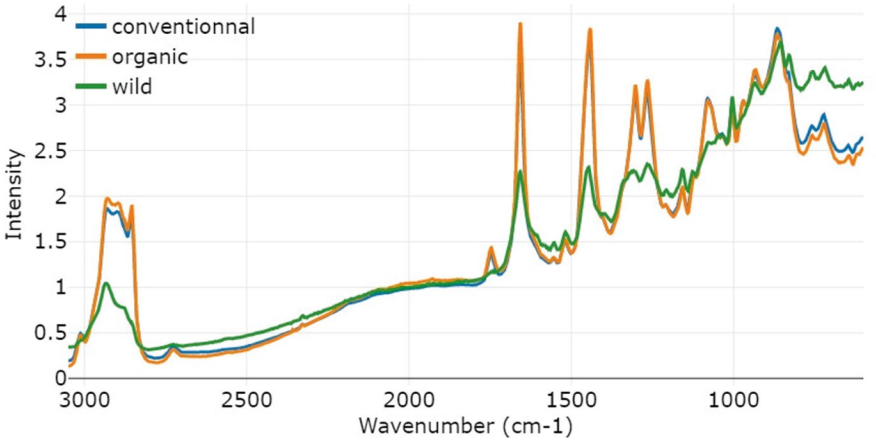

Fig. 5.7 Comparison of the Raman spectra after normalisation of wild and farmed (conventional and organic) salmon that have been frozen and ground. Spectra were acquired using a Raman spectrometer Senterra II (Bruker) with a laser of 785 nm

in crops, grain or nuts (Gabbitas et al. 2023; Wu et al. 2021; Zhai et al. 2021; Jia et al. 2020; Liu et al. 2009) to heavy metals like lead, cadmium, arsenic, or mercury in food detected with SERS (Guo et al. 2023). Also, Raman can be used for identifying and differentiating bacterial strains (Dib et al. 2023; Huayhongthong et al. 2019; Zhao et al. 2018) or to analyse banned food additives by RRS (Shadi et al. 2008). Raman has been also used for monitoring shelf stability, i.e. the technique may help for assessing changes in food composition over time, allowing for real-time monitoring of shelf stability, spoilage, or degradation processes. For instance, SORS has been used for the monitoring of the alcoholic fermentation process of white wine (Schorn-García et al. 2023), but Raman can also help in optimizing storage conditions and shelf life (Logan et al. 2022; Sun et al. 2022; Liu et al. 2020; Wang et al. 2014)).

4.2 Raman for Authenticity and Traceability Issues

The use of Raman for issues related to authenticity and traceability includes studies for the characterization of food fraud, offering a reliable method for detecting and identifying adulteration, counterfeit products, and misrepresentation within the food industry (Abbas et al. 2020; Vermeulen et al. 2017). The technique's ability to provide unique molecular fingerprints enables the differentiation between authentic and fraudulent food products, contributing significantly to ensuring food authenticity and consumer protection. It can detect counterfeit products, such as fake wines or counterfeit pharmaceuticals, by comparing their spectral signatures against authentic references (Boyaci et al. 2014; Nunes et al. 2019). Raman spectroscopy creates characteristic spectral patterns specific to each food component. When applied to authentic food samples, it generates reference spectra that serve as benchmarks. Any deviations or differences observed in the spectra of suspect samples indicate potential adulteration or fraud. In this sense, the ability of the spatially offset Raman spectroscopy (SORS) to analyse samples through a container makes it an effective tool for the study of beverage products, such as the authentication of spirits (Pérez-Beltran et al. 2022) or the distinction of cheeses according to animal species (Ostovar et al. 2021), among others. Raman spectroscopy helps also in the detection of adulterants or substitutes in various food products. It assists in detecting adulterants or substitutions in high-value food products. For instance, it can differentiate between pure and adulterated honey, authentic and counterfeit beverages and dry milk (Qin et al. 2013), counterfeit spices (Dhakal et al. 2016), adulterated pistachios (Taylan et al. 2021) or adulterated or enriched eggs (Mendes et al. 2019). Figure 5.8 shows representative Raman spectra obtained for egg yolk from hens fed with different diets.

In the case of edible oils, it can distinguish between pure and adulterated oils by detecting the presence of cheaper oils or non-edible substances (Zhao et al. 2022; Jin et al. 2021). Moreover, Raman could be a good tool for the verification of the geographical origins of food products (Tena et al. 2019). For instance, different

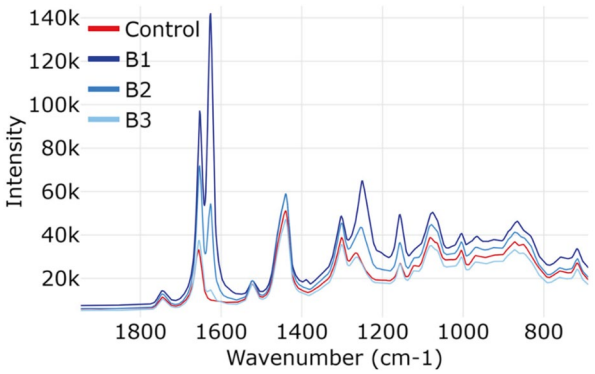

Fig. 5.8 Mean Raman spectra (laser at 785 nm) of two types of eggs: in red, Raman spectra of egg yolk from hens fed a normal diet (control); in blue: egg yolk from hens fed an enhanced diet (rich in polyphenols and fat) at different dates (B1: day 1; B2: day 5; B3: day 10). The upper graph represents the intensity variation of the bands in the vicinity of 1626 cm^{-1} for different egg yolks. After a certain point, a return to normal is observed, i.e. there is a reduction in the effect of the enhanced diet on egg quality. Spectra were acquired using a Raman spectrometer Senterra II (Bruker) with a laser of 785 nm (Baeten, Arnould, Fernández & Larondelle, unpublished data)

regions produce wines with unique chemical compositions, and Raman spectroscopy can differentiate between these regions, aiding in verifying the authenticity of wine labels. Also, for the origin of fish (Ren et al. 2023), essential oils (Almeida et al. 2013), honey (Damiani et al. 2020) or argan oils (El Maouardi et al. 2023), among others. With its ability to provide accurate chemical fingerprints, Raman spectroscopy aids in ensuring compliance with labelling regulations and certifications, verifying claims related to organic, natural, or specific product characteristics. Raman can be used for simultaneous identification of different components in a mixture and estimation of their concentrations for authentication or quantitative inspection purposes (Dhakal et al. 2017).

5 Two Applications of Raman Spectroscopy for Quality Control and Its Use for Authenticity and Traceability Issues

5.1 Pesticide Characterization and Fraud in Pesticides

Raman spectroscopy enables the rapid screening of fruits, vegetables, and grains for the presence of harmful chemicals used in agricultural practices, ensuring compliance with safety standards. In the literature, Raman spectroscopy has proven to be a valuable tool in characterizing pesticides, detect and quantify pesticide residues in food products as well as detecting potential fraud or adulteration in these chemical compounds (Zhai et al. 2016; Dhakal et al. 2014). Its application in this domain

involves identifying and analysing the molecular structure of pesticides, allowing for precise characterization and verification of their authenticity.

Raman spectroscopy provides unique molecular fingerprints for different pesticides. It identifies characteristic spectral patterns based on the vibrational modes of the chemical bonds present in the pesticide molecules. In addition, it helps to determine the chemical composition, functional groups and structural properties of pesticides. This information helps to identify and differentiate different types of pesticides. It also allows for quantitative analysis, enabling the determination of pesticide concentrations in formulations or environmental samples. In this context, it is a good technique for pesticide formulations (Skoulika et al. 2000) or for the detection of pesticide residues in food products (Sato Berrú et al. 2004; Xu et al. 2017; Luna Hernández 2018; Rocío and Mariel 2019; Dowgiallo and Guenther 2019; Zhang et al. 2021; Pham et al. 2022). Figure 5.9 shows an example of the application of a data visualization algorithm (t-SNE) applied on Raman spectra of different pesticide formulations commonly used in apple fruits. It shows the potential of the technique to discriminate and therefore, characterize pesticide formulations.

Moreover, Dias et al. constructed a database with Raman spectra of the main commercial pesticides currently used and they make it available to the scientific community (Dias et al. 2019). Raman can also detect adulteration or the presence of unauthorized or harmful substances in pesticide formulations. By comparing the spectral signatures of authentic pesticides with suspect samples, it can reveal inconsistencies or deviations indicative of adulteration or fraud. Manufacturers often add marker compounds or unique chemical signatures to authentic pesticides. Raman

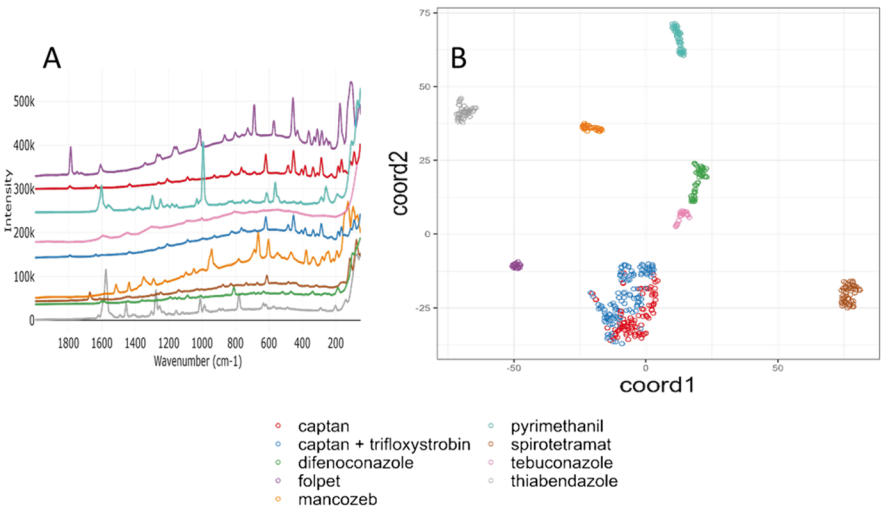

Fig. 5.9 (**a**) Raman spectra of 9 different pure pesticide formulations acquired using a Raman spectrometer Senterra II (Bruker) with a laser of 785 nm. (**b**) t-SNE representation of the individual spectra of the 9 pure pesticide formulations

spectroscopy can verify the presence of these markers, ensuring the authenticity of the product.

As conclusion, Raman spectroscopy serves as a valuable tool for characterizing pesticides and detecting potential fraud or adulteration in these chemical compounds. Its ability to provide rapid, non-destructive analysis with high sensitivity makes it a promising technique in ensuring the authenticity and safety of pesticides, thereby contributing to the overall integrity of agricultural practices and food production. Moreover, samples can be analysed through transparent containers avoiding contact with the toxic substances. In addition, by using the light as an analyser, it allows opening new possibilities of detecting contaminants on site, as for instance, through the implementation of a portable Raman equipment. In this direction, in the last years we assist to the emergence of handheld spectroscopic devices allowing bringing the laboratory to the sample (lab to the sample approach).

However, the Raman technology may not be applicable for sensitive detection due to the inherently weak Raman signals. For this reason, alternatives solutions have been proposed using surface-enhanced Raman scattering (SERS) (Marino-Lopez et al. 2019; Ogundare and van Zyl 2019; Bodelón and Pastoriza-Santos 2020). In the case of fruits, the detection of pesticides by using different nanostructures for SERS has been largely studied at the literature. Liu et al. studied three types of pesticides (carbaryl, phosmet, and azinphos-methyl) widely used in apples and tomatoes using SERS coupled with gold nanaostructure with detection limits meeting the maximum residue limits established by Food and Agriculture Organization of the United Nations and World Health Organization (Liu et al. 2012). Pang et al. performed a complete review of SERS detection of some synthetic commercial chemical pesticides (Pang et al. 2016). More recently, Mikac et al. studied the detection of glyphosate by SERS using gold and silver nanoparticles and three different commonly used laser excitations of a Raman microscope complemented with a portable Raman spectrometer. Emonds-Alt et al. also demonstrated the capability of SERS for detecting glyphosate and its main metabolite AMPA in water (Emonds-Al et al. 2022). In their review, Terry et al., highlight the characteristics of effective SERS nanosubstrates, and explore methods for the SERS detection of pesticides, among other products affecting the environment. In their work, they encourage researchers to continuing study the SERS technology to assure that it can be implemented in a real-world environment more effectively and efficiently, ultimately providing reliable and timely data to help and make science-based strategies and policies to protect environmental safety and public health (Terry et al. 2022).

Ongoing research focuses on improving Raman spectroscopy‘s sensitivity, especially for trace-level detection, and addressing challenges related to sample heterogeneity and interference from formulation matrices. Advances in instrumentation and data analysis techniques aim to enhance its capabilities for more comprehensive and accurate pesticide analysis and fraud detection.

5.2 *Detection of Adulteration of Edible Vegetable Oils*

Raman spectroscopy has also emerged as a powerful technique for detecting adulteration in edible vegetable oils, providing a reliable method to identify various types of adulterants or substitutions that might compromise the quality and authenticity of these oils. In this context, the main concern is the identification of oil components, i.e. to differentiate between pure vegetable oils and adulterated or blended oils by identifying the characteristic spectral fingerprints of various oil components such as triglycerides, fatty acids, and unsaponifiable matter (Baeten et al. 1998; Aparicio 1998; Baeten et al. 2001). Then, the adulterants commonly used to dilute or substitute expensive oils, such as lower-grade oils, recycled oils, or non-edible oils must be identified. Raman spectroscopy can distinguish between the spectral signatures of different oils, revealing any deviations from the expected composition (Abbas et al. 2009). Figure 5.10 shows the Raman spectra of five different oils, highlighting the spectral differences between them. These differences are represented in the form of characteristic spectral bands for each oil, thus allowing a clear discrimination between them and possible detection in case of contamination.

Raman has been also used for the characterization of essential oils (Vargas Jentzsch and Ciobotă 2014; Jentzsch et al. 2015; Vargas Jentzsch et al. 2018) and is becoming the technique of choice for the characterization of edible oils. Olive oil is usually more expensive than other oils due to its high contents of vitamins and antioxidants (Bian et al. 2022). Many studies based on Raman have focused on the quantitative analysis of olive oils. Advance Raman modalities have also been used in extra olive oil, as Resonant Raman spectroscopy (RRS) for the investigation of changes in carotenoid concentration as it oxidizes under accelerated thermal aging

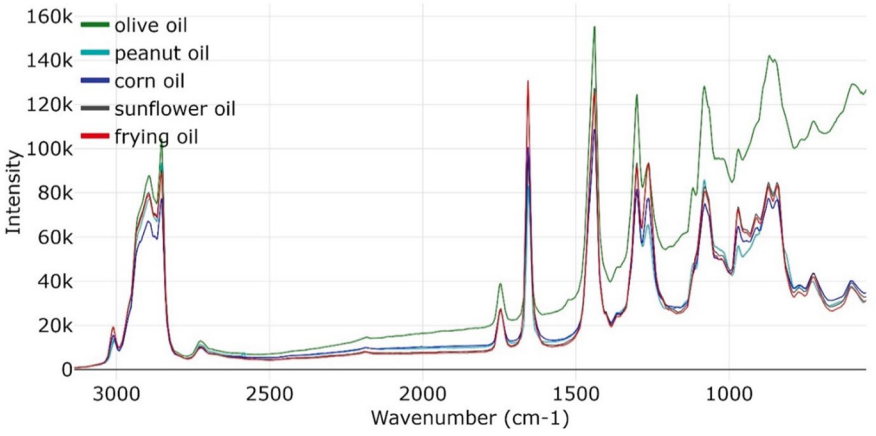

Fig. 5.10 Raman spectra of five different types of oils (olive, peanut, corn, sunflower and frying oils). Spectra were acquired using a Raman spectrometer Senterra II (Bruker) with a laser of 785 nm

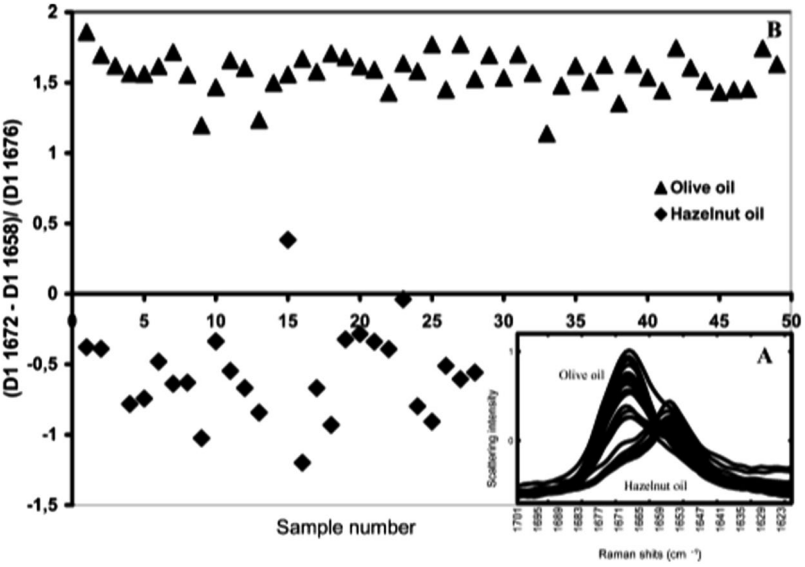

Fig. 5.11 FT-Raman spectra of the unsaponifiable matter of hazelnut and olive oils (**a**) and classification of the samples (**b**) obtained with the rule based on three Raman shifts (1676 1672, and 1658 cm^{-1}) (Baeten et al. 2005)

(Curran Eggertson and Venturini 2023), or SERS for the monitoring of bioactive components (Camerlingo et al. 2019). However, there is no official analytical methods for the detection of olive oil adulteration (Georgouli et al. 2017). The adulteration of olive oil with other edible oils can be of three ways: blends of virgin oils, blends of refined oils, and blends of virgin and refined oils. Typical cases comprise the adulteration of virgin olive oils with hazelnut (Fig. 5.11) (Baeten et al. 1996; Lopez-Diez et al. 2003; Baeten et al. 2005), with soybean oil (Mendes et al. 2015), or the adulteration of sesame oil with cheaper oils (Teng et al. 2024), among others.

In addition to qualitative analysis, Raman allows for quantitative assessment by measuring the concentrations of different components in the oils, aiding in determining the extent of adulteration. Studies in the literature referred to the quantitative analysis of garlic (Allium sativum) oil unsaturated acyclic components (Kimbaris et al. 2006), the determination of rapeseed and corn oils in olive oils (De Lima et al. 2020), the estimation of the proportion of waste cooking oil in olive oil (Li et al. 2018) and the quantification of blended oils (Dong et al. 2017; Jimenez-Carvelo et al. 2017; Bian et al. 2022; Fan et al. 2022).

However, challenges in the use of Raman for edible oil analysis include issues related to sample variability and the complexity of oil matrices. Research focuses on addressing these challenges by improving data analysis methods and the instrument sensitivity, as well as developing robust reference databases to enhance the accuracy and reliability of the technique.

6 Conclusion

In conclusion, Raman spectroscopy stands as a valuable tool in ensuring food safety, quality, and authenticity. Its ability to provide rapid and non-destructive analysis makes it an indispensable technology for food producers, regulatory bodies and consumers in maintaining high standards and trust in the food supply chain. As advancements continue, its role in food analysis and verification will likely expand, further cementing its significance in the food industry. Despite its advantages, Raman spectroscopy does face limitations, including issues with fluorescence interference and sample preparation complexities. Researchers are continuously working on improving the technique's sensitivity, reducing interference, data processing techniques and developing portable and user-friendly devices to expand its practical applications in the food industry.

References

Abbas O, Fernández Pierna JA, Codony R, von Holst C, Baeten V (2009) Assessment of the discrimination of animal fat by FT-Raman spectroscopy. J Mol Struct 924–926:294–300. https://doi.org/10.1016/j.molstruc.2009.01.027

Abbas O, Pissard A, Baeten V (2020) Near-infrared, mid-infrared, and Raman spectroscopy. In: Pico Y (ed) Chemical analysis of food: techniques and applications. Elsevier Science, Burlington, pp 77–134. https://doi.org/10.1016/B978-0-12-813266-1.00003-6

Almeida MR, Fidelis CHV, Barata LES, Poppi RJ (2013) Classification of Amazonian rosewood essential oil by Raman spectroscopy and PLS-DA with reliability estimation. Talanta 117:305–311. https://doi.org/10.1016/j.talanta.2013.09.025

Aparicio R (1998) Authentication of virgin olive oil by FT-MIR and FT-Raman spectroscopy; project FAIR CT1996-5053. The Commission of the European Communities 1998

Baeten V, Meurens M, Morales MT, Aparicio R (1996) Detection of virgin olive oil adulteration by Fourier transform Raman spectroscopy. J Agric Food Chem 44:2225–2230. https://doi.org/10.1021/jf9600115

Baeten V, Hourant P, Morales MT, Aparicio R (1998) Oils and fats classification by Fourier transform Raman spectroscopy. Agric Food Chem 46(7):2638–2646. https://doi.org/10.1021/jf9707851

Baeten V, Dardenne P, Aparicio R (2001) Interpretation of Fourier transform Raman spectra of the unsaponifiable matter in a selection of edible oils. J Agric Food Chem 49:5098–5107. https://doi.org/10.1021/jf010146x

Baeten V, Fernández Pierna JA, Dardenne P, Meurens M, García González DL, Aparicio Ruiz R (2005) Detection of the presence of hazelnut oil in olive oil by FT-Raman and FT-MIR spectroscopy. J Agric Food Chem 53:6201–6206. https://doi.org/10.1021/jf050595n

Banwell CN, McCash EM (1994) Raman spectroscopy. In: Fundamentals of molecular spectroscopy, 4rd edn. McGraw-Hill Companies, pp 124–155

Baranska M, Schulz H, Rösch P, Strehle M, Popp J (2004) Identification of secondary metabolites in medicinal and spice plants by NIR-FTRaman microspectroscopic mapping. Analyst 129:926930. https://doi.org/10.1039/B408933M

Baranska M, Schulz H, Joubert E, Manley M (2006) In situ flavonoid analysis by FT-Raman spectroscopy: identification, distribution, and quantification of aspalathin in green rooibos (Aspalathus linearis). Anal Chem 78:7716–7721. https://doi.org/10.1021/ac061123q

Beganović A, Hawthorne LM, Bach K, Huck CW (2019) Critical review on the utilization of handheld and portable Raman spectrometry in meat science. Food Secur 8(2):49. https://doi.org/10.3390/foods8020049

Bian X, Wang Y, Wang S, Johnson JB, Sun H, Guo Y, Tan X (2022) A review of advanced methods for the quantitative analysis of single component oil in edible oil blends. Food Secur 11(16):2436. https://doi.org/10.3390/foods11162436

Bodelón G, Pastoriza-Santos I (2020) Recent Progress in surface-enhanced Raman scattering for the detection of chemical contaminants in water. Front Chem 8:478. https://doi.org/10.3389/fchem.2020.00478

Boyaci IH, Temiz HT, Uysal RS, Velioglu HM, Yadegari RJ, Rishkan MM (2014) A novel method for discrimination of beef and horsemeat using Raman spectroscopy. Food Chem 148:37–41. https://doi.org/10.1016/j.foodchem.2013.10.006

Camerlingo C, Portaccio M, Delfino I, Lepore M (2019) Surface-enhanced Raman spectroscopy for monitoring extravirgin olive oil bioactive components. J Chem 2019:9537419. https://doi.org/10.1155/2019/9537419

Chen J, Lv J, Wei J, Shum PP, Chen GJ (2023) Raman spectroscopy in food safety: a mini review. Glob J Nutr Food Sci 4(3). https://doi.org/10.1016/bs.afnr.2023.03.007

Curran Eggertson E, Venturini F (2023) Resonant Raman spectroscopy of carotenoids in aging of extra olive oil. Sensors 23(17):7621. https://doi.org/10.3390/s23177621

Damiani T, Alonso Salces RM, Aubone I, Baeten V, Arnould Q, Dall'Asta C, Fuselli SR, Fernández Pierna JA (2020) Vibrational spectroscopy coupled to a multivariate analysis tiered approach for Argentinean honey provenance confirmation. In: Delahaut P, Marega R (eds) Novel analytical methods in food analysis. MDPI. https://doi.org/10.3390/foods9101450

De Lima TK, Musso M, Menezes DB (2020) Using Raman spectroscopy and an exponential equation approach to detect adulteration of olive oil with rapeseed and corn oil. Food Chem 333:127454. https://doi.org/10.1016/j.foodchem.2020.127454

Dhakal S, Li Y, Peng Y, Chao K, Qin J, Guo L (2014) Prototype instrument development for non-destructive detection of pesticide residue in apple surface using Raman technology. J Food Eng 123:94–103. https://doi.org/10.1016/j.jfoodeng.2013.09.025

Dhakal S, Chao K, Schmidt W, Qin J, Kim M, Chan D (2016) Evaluation of turmeric powder adulterated with metanil yellow using FT-Raman and FT-IR spectroscopy. Food Secur 5:36. https://doi.org/10.3390/foods5020036

Dhakal S, Chao K, Qin J, Kim M, Peng Y, Chan D (2017) Identification and evaluation of composition in food powder using point-scan Raman spectral imaging. Appl Sci 7(1):1. https://doi.org/10.3390/app7010001

Dias LAF, Jussiani EI, Appoloni CR (2019) Reference Raman spectral database of commercial pesticides. J Appl Spectrosc. https://doi.org/10.1007/s10812-019-00798-1

Dib O, Assaf A, Grangé E, Morin JF, Cordella C, Thouand G (2023) Chemometrics tools for the non-targeted research of food bacteria by Raman spectroscopy. https://doi.org/10.2139/ssrn.4347438

Dietzek B, Cialla D, Schmitt M, Popp J (2010) Introduction to the fundamentals of Raman spectroscopy. In: Dieing T, Hollricher O, Toporski J (eds) Confocal Raman microscopy. Springer

Dong JJ, Wu JZ, Chen Y, Liu CL, Chen LG (2017) Rapid quantitative determination of raw material components in blended edible oil based on Raman spectroscopy. Trans Chin Soc Agric 48:417–421+428. https://doi.org/10.1007/978-3-642-12522-5_2

Dowgiallo AM, Guenther DA (2019) Determination of the limit of detection of multiple pesticides utilizing gold nanoparticles and surface-enhanced Raman spectroscopy. J Agric Food Chem 67(46):12642–12651. https://doi.org/10.1021/acs.jafc.9b01544

El Maouardi M, Alaoui Mansouri M, De Braekeleer K, Bouklouze A, Vander Heyden Y (2023) Evaluation of multivariate filters on vibrational spectroscopic fingerprints for the PLS-DA and SIMCA classification of Argan oils from four Moroccan regions. Molecules 28:5698. https://doi.org/10.3390/molecules28155698

Emonds-Al G, Malherbe C, Kasemiire A, Avohou HT, Hubert P, Ziemons E, Monbaliu JC, Eppe G (2022) Development and validation of an integrated microfluidic device with an in-line Surface Enhanced Raman Spectroscopy (SERS) detection of glyphosate in drinking water. Talanta 249:123640. https://doi.org/10.1016/j.talanta.2022.123640

Esmonde-White K, Lewis M, Perilli T, Della Vedova T, Lewis I (2022) Raman spectroscopy in analysing fats and oils in foods. Spectroscopy 37(s6):34–45. https://doi.org/10.56530/spectroscopy.jb8390i4

Fan D, Huang W, Cheng-yi Liu T, Zhang X, Li W, Gao X, Meng Y (2022) Quantitative analysis of blended oils by confocal Raman spectroscopy and chemometrics in situ. Food Control 142:109244

Fernández Pierna JA, Abbas O, Dardenne P, Baeten V (2011) Discrimination of Corsican honey by FT-Raman spectroscopy and chemometrics. Biotechnologie, Agronomie, Société et Environnement 15(1):75–84. https://popups.uliege.be/1780-4507/index.php?id=6895

Ferraro JR (2003) Introductory Raman spectroscopy, 2nd edn. Academic Press. https://doi.org/10.1016/j.foodcont.2022.109244

Gabbitas A, Ahlborn G, Allen K, Pang S (2023) Advancing mycotoxin detection: multivariate rapid analysis on corn using surface enhanced Raman spectroscopy (SERS). Toxins 15(10):610. https://doi.org/10.3390/toxins15100610

Georgouli K, Martinez Del Rincon J, Koidis A (2017) Continuous statistical modelling for rapid detection of adulteration of extra virgin olive oil using mid infrared and Raman spectroscopic data. Food Chem 217:735–742. https://doi.org/10.1016/j.foodchem.2016.09.011

Guo Z, Chen P, Yosri N, Chen Q, Elseedi HR, Zou X, Yang H (2023) Detection of heavy metals in food and agricultural products by surface-enhanced Raman spectroscopy. Food Rev Intl 39(3):1440–1461. https://doi.org/10.1080/87559129.2021.1934005

Herrero AM (2008) Raman spectroscopy a promising technique for quality assessment of meat and fish: a review. Food Chem 107:1642–1651. https://doi.org/10.1016/j.foodchem.2007.10.014

Huayhongthong S, Khuntayaporn P, Thirapanmethee K, Wanapaisan P, Chomnawang M (2019) Raman spectroscopic analysis of food-borne microorganisms. LWT 114:108419. https://doi.org/10.1016/j.lwt.2019.108419

Jensen IJ, Eliertsen KE, Almli Otnaes CH, Maehre HK, Elvevoll EO (2020) An update on the content of fatty acids, dioxins, PCBs and heavy metals in farmed, escaped and wild Atlantic Salmon (Salmo salar L.) in Norway. Foods 9(12):1901. https://doi.org/10.3390/foods9121901

Jentzsch PV, Ramos LA, Ciobotă V (2015) Handheld Raman spectroscopy for the distinction of essential oils used in the cosmetics industry. Cosmetics 2:162–176. https://doi.org/10.3390/cosmetics2020162

Jia B, Wang W, Ni XZ, Chu X, Yoon SC, Lawrence KC (2020) Detection of mycotoxins and toxigenic fungi in cereal grains using vibrational spectroscopic techniques: a review. World Mycotoxin J 13(2):163–177. https://doi.org/10.3920/WMJ2019.2510

Jimenez-Carvelo AM, Osorio MT, Koidis A, Gonzalez-Casado A, Cuadros-Rodrigue L (2017) Chemometric classification and quantification of olive oil in blends with any edible vegetable oils using FTIR-ATR and Raman spectroscopy. LWT-Food Sci Technol 86:174–184. https://doi.org/10.1016/j.lwt.2017.07.050

Jin H, Li H, Yin Z, Zhu Y, Lu A, Zhao D, Li C (2021) Application of Raman spectroscopy in the rapid detection of waste cooking oil. Food Chem 362:130191. https://doi.org/10.1016/j.foodchem.2021.130191

Kimbaris AC, Siatis NG, Pappas CS, Tarantilis PA, Daferera DJ, Polissiou MG (2006) Quantitative analysis of garlic (Allium sativum) oil unsaturated acyclic components using FT-Raman spectroscopy. Food Chem 94(2):287–295. https://doi.org/10.1016/j.foodchem.2005.01.017

Kuhar N, Sil S, Umapathy S (2021) Potential of Raman spectroscopic techniques to study proteins. Spectrochim Acta A Mol Biomol Spectrosc 258:119712. https://doi.org/10.1016/j.saa.2021.119712

Larkin PJ (2018) Infrared and Raman spectroscopy: principles and spectral interpretation, 2nd edn. Elsevier

Le Ru EC, Etchegoin PG (2009) Principles of surface-enhanced Raman spectroscopy. Elsevier. https://doi.org/10.1016/B978-0-444-52779-0.X0001-3

Li YP, Fang T, Zhu SQ, Huang FR, Chen ZQ, Wan Y (2018) Detection of olive oil adulteration with waste cooking oil via Raman spectroscopy combined with iPLS and SiPLS. Spectrochim Acta A 189:37–43. https://doi.org/10.1016/j.saa.2017.06.049

Lin DY, Yu CY, Ku CA, Chung CK (2023) Design, fabrication, and applications of SERS substrates for food safety detection: review. Micromachines 14(7):1343. https://doi.org/10.3390/mi14071343

Liu Y, Delwiche SR, Dong Y (2009) Feasibility of FT–Raman spectroscopy for rapid screening for DON toxin in ground wheat and barley. Food Addit Contam Part A 26(10):1396–1401. https://doi.org/10.1080/02652030903013310

Liu B, Zhou P, Liu X, Sun X (2012) Detection of pesticides in fruits by surface-enhanced Raman spectroscopy coupled with gold nanostructures. Food Bioprocess Technol 6(3). https://doi.org/10.1007/s11947-011-0774-5

Liu Y, Ren X, Yu H, Cheng Y, Guo Y, Yao W, Xie Y (2020) Non-destructive and online egg freshness assessment from the egg shell based on Raman spectroscopy. Food Control 118:107426. https://doi.org/10.1016/j.foodcont.2020.107426

Liu Z, Yang Y, Huang M, Zhu Q (2023) Spatially offset Raman spectroscopy combined with attention-based LSTM for freshness evaluation of shrimp. Sensors 23(5). https://doi.org/10.3390/s23052827

Logan BG, Hopkins DL, Schmidtke LM, Fowler SM (2022) Assessing chemometric models developed using Raman spectroscopy and fatty acid data for Northern and Southern Australian beef production systems. Meat Sci 187:108753. https://doi.org/10.1016/j.meatsci.2022.108753

Lopez-Diez EC, Bianchi G, Goodacre R (2003) Rapid quantitative assessment of the adulteration of virgin olive oils with hazelnut using Raman spectroscopy and chemometrics. J Agric Food Chem 51:6145–6150. https://doi.org/10.1021/jf034493d

Luna Hernández I (2018) Detección de residuos de glifosato de maíz mediante espectroscopía Raman de superficie aumentada. PhD thesis at the University of Puebla (Mexico)

Marino-Lopez A, Sousa-Castillo A, Blanco-Formoso M, Furini LN, Rodriguez-Lorenzo L, Pazos-Perez N (2019) Microporous plasmonic capsules as stable molecular sieves for direct SERS quantification of small pollutants in natural waters. Chemnanomat 5:46–50. https://doi.org/10.3389/fchem.2020.00478

McCreery RL (2001) Raman spectroscopy for chemical analysis. Wiley. https://doi.org/10.1002/0471721646

Mendes TO, da Rocha RA, Porto BLS, de Oliveira MAL, dos Anjos VC, Bell MJV (2015) Quantification of extra-virgin olive oil adulteration with soybean oil: a comparative study of NIR, MIR, and Raman spectroscopy associated with chemometric approaches. Food Anal Methods 8:2339–2346. https://doi.org/10.1007/s12161-015-0121-y

Mendes TO, Porto BLS, Almeida MR, Fantini C, Sena MM (2019) Discrimination between conventional and omega-3 fatty acids enriched eggs by FT-Raman spectroscopy and chemometric tools. Food Chem 273:144–150. https://doi.org/10.1016/j.foodchem.2017.12.084

Morey R, Ermolenkov A, Payne WZ, Scheuring DC, Koym JW, Vales MI, Kurouski D (2020) Non-invasive identification of potato varieties and prediction of the origin of tuber cultivation using spatially offset Raman spectroscopy. Anal Bioanal Chem 412(19):4585–4594. https://doi.org/10.1007/s00216-020-02706-5

Mosca S, Conti C, Stone N, Matousek P (2021) Spatially offset Raman spectroscopy. Nat Rev Methods Primers 1:21. https://doi.org/10.1021/acs.analchem.1c00490

Mosier-Boss PA (2017) Review of SERS substrates for chemical sensing. Nano 7(6):142. https://doi.org/10.3390/nano7060142

Nunes KM, Vinícius M, Andrade O, Almeida MR, Fantini C, Sena MM (2019) Raman spectroscopy and discriminant analysis applied to the detection of frauds in bovine meat by the addition of salts and carrageenan. Microchem J 147:582–589. https://doi.org/10.1016/j.microc.2019.03.076

Ogundare SA, van Zyl WE (2019) A review of cellulose-based substrates for SERS: fundamentals, design principles, applications. Cellulose 26:6489–6528. https://doi.org/10.1007/s10570-019-02580-0

Ostovar S, Afshari R, Landry J, Pillidge C, Gill H, Blanch E (2021) Spatially offset Raman spectroscopy: a convenient and rapid tool to distinguish cheese made with milks from different animal species. J Raman Spectrosc 52(10):1705–1711. https://doi.org/10.1002/jrs.6179

Pang S, Yang T, He L (2016) Review of surface enhanced raman spectroscopic (SERS) detection of synthetic chemical pesticides. Trends Anal Chem., S0165993616300218. https://doi.org/10.1016/j.trac.2016.06.017

Pérez-Beltran CH, Pérez-Caballero G, Andrade JM, Cuadros-Rodríguez L, Jiménez-Carvelo AM (2022) Non-targeted spatially offset Raman spectroscopy-based vanguard analytical method to authenticate spirits: white tequilas as a case study. Microchem J 183:108126. https://doi.org/10.1016/j.microc.2022.108126

Petersen M, Yu Z, Lu X (2021) Application of Raman spectroscopic methods in food safety: a review. Biosensors 11(6):187. https://doi.org/10.3390/bios11060187

Pham UT, Phan QHT, Nguyen LP, Luu PD, Doan TD, Trinh HT, Dinh CT, Nguyen TV, Tran TQ, Le DX (2022) Rapid quantitative determination of multiple pesticide residues in mango fruits by surface-enhanced Raman spectroscopy. PRO 10(3):442. https://doi.org/10.3390/pr10030442

Pompeu DR, Larondelle Y, Rogez H, Abbas O, Fernández Pierna JA, Baeten V (2018) Characterization and discrimination of phenolic compounds using Fourier transform Raman spectroscopy and chemometric tools. Biotechnol Agron Soc Environ 22(1):13–28. https://doi.org/10.25518/1780-4507.16270

Qin J, Chao K, Kim MS (2013) Simultaneous detection of multiple adulterants in dry milk using macro-scale Raman chemical imaging. Food Chem 138:998–1007. https://doi.org/10.1016/j.foodchem.2012.10.115

Qin J, Kim MS, Chao K, Schmidt WF, Dhakal S, Cho BK, Peng Y, Huang M (2017) Subsurface inspection of food safety and quality using line-scan spatially offset Raman spectroscopy technique. Food Control 75:246–254. https://doi.org/10.1016/j.foodcont.2016.12.012

Ren L, Tian Y, Yang X, Wang Q, Wang L, Geng X, Wang K, Du Z, Li Y, Lin H (2023) Rapid identification of fish species by laser-induced breakdown spectroscopy and Raman spectroscopy coupled with machine learning methods. Food Chem 400:134043. https://doi.org/10.1016/j.foodchem.2022.134043

Rocío LA, Mariel RR (2019) Implementación de nuevas técnicas de detección ultrasensible de residuos de pesticidas en cáscara de frutas y vegetales. Investigación Joven 6

Sato Berrú RY, Medina Gutiérrez C, Medina Valtierra J, Frausto Reyes C (2004) Aplicación de la espectroscopia Raman para la caracterización de pesticidas orgánicos. Revista Internacional de Contaminación Ambiental 20(1):17–24

Schorn-García D, Ezenarro J, Aceña L, Busto O, Boqué R, Giussani B, Mestres M (2023) Spatially offset Raman spectroscopic (SORS) analysis of wine alcoholic fermentation: a preliminary study. Fermentation 9(2):115. https://doi.org/10.3390/fermentation9020115

Shadi I, Schuler S, Warner ME, Jarvis R, Goodacre R (2008) Analysis of banned food additives (e numbers) by surface enhanced (resonance) Raman spectroscopy using gold nano-particles. MIB Interdisciplinary Research Conference

Skoulika SG, Georgiou CA, Polissiou MG (2000) FT-Raman spectroscopy — analytical tool for routine analysis of diazinon pesticide formulations. Talanta 51(3):599–604. https://doi.org/10.1016/S0039-9140(99)00336-7

Smith E, Dent G (2019) Modern Raman spectroscopy: a practical approach, 2nd edn. Wiley

Socrates G (2004) Infrared and Raman characteristic group frequencies: tables and charts, 3rd edn. Wiley

Stiles PL, Deringer JA, Shah NC, Van Duyne RP (2008) Surface-enhanced Raman spectroscopy. Annu Rev Anal Chem 1:601–626. https://doi.org/10.1146/annurev.anchem.1.031207.112814

Stocco G, Gómez-Mascaraque LG, Deshwal GK, Cruz Sanchez J, Molle A, Pizzamiglio V, Berzaghi P, Gergov G, Cipolat-Gotet C (2024) Exploring the use of NIR and Raman spectroscopy for the prediction of quality traits in PDO cheeses. Front Nutr 11. https://doi.org/10.3389/fnut.2024.1327301

Sun Y, Tang H, Zou X, Meng G, Wu N (2022) Raman spectroscopy for food quality assurance and safety monitoring: a review. Curr Opin Food Sci 47:100910. https://doi.org/10.1016/j.cofs.2022.100910

Taylan O, Cebi N, Yilmaz MT, Sagdic O, Ozdemir D, Balubaid M (2021) Rapid detection of green-pea adulteration in pistachio nuts using Raman spectroscopy and chemometrics. J Sci Food Agric 101:1699–1708. https://doi.org/10.1002/jsfa.10845

Tena N, Aparicio R, Baeten V, Garcia-Gonzalez DL, Fernandez-Pierna JA (2019) Assessment of vibrational spectroscopy performance in geographical identification of virgin olive oils: a world level study. Eur J Lipid Sci Technol. https://doi.org/10.1002/ejlt.201900035

Teng Y, Chen Y, Chen X, Zuo S, Li X, Pan Z, Shao K, Du J, Li Z (2024) Revealing the adulteration of sesame oil products by portable Raman spectrometer and 1D CNN vector regression: a comparative study with chemometrics and colorimetry. Food Chem 436:137694. https://doi.org/10.1016/j.foodchem.2023.137694

Terry LR, Sanders S, Potoff RH, Kruel JW, Jain M, Guo H (2022) Applications of surface-enhanced Raman spectroscopy in environmental detection. Anal Sci Adv 3(3–4):113–145. https://doi.org/10.1002/ansa.202200003

Vandenabeele P (2013) Practical Raman spectroscopy—an introduction. Wiley. https://doi.org/10.1002/9781119961284

Vandenabeele P, Edwards HGM, Jehlička J (2014) The role of mobile instrumentation in novel applications of Raman spectroscopy: archaeometry, geosciences, and forensics. Chem Soc Rev 43:2628–2649. https://doi.org/10.1039/C3CS60263J

Vargas Jentzsch P, Ciobotă V (2014) Raman spectroscopy as an analytical tool for analysis of vegetable and essential oils. Flavour Fragr J 29:287–295. https://doi.org/10.1002/ffj.3203

Vargas Jentzsch P, Gualpa F, Ramos LA, Ciobotă V (2018) Adulteration of clove essential oil: detection using a handheld Raman spectrometer. Flavour Fragr J 33:184–190. https://doi.org/10.1002/ffj.3438

Vermeulen P, Fernández Pierna JA, Abbas O, Rogez H, Davrieux F, Baeten V (2017) Authentication and traceability of agricultural and food products using vibrational spectroscopy. In: Montet D, Ray RC (eds) Food traceability and authenticity: analytical techniques, Biology series. CRC Press, p 450. https://doi.org/10.1201/9781351228435

Wang Q, Li Z, Ma Z, Liang L (2014) Real time monitoring of multiple components in wine fermentation using an on-line auto-calibration Raman spectroscopy. Sens Actuators B Chem 202:426–432. https://doi.org/10.1016/j.snb.2014.05.109

Wang X, Huang SC, Hu S, Yan S, Ren B (2020) Fundamental understanding and applications of plasmon-enhanced Raman spectroscopy. Nat Rev Phys 2:253–271. https://doi.org/10.1038/s42254-020-0171-y

Wang K, Li Z, Li J, Lin H (2021) Raman spectroscopic techniques for nondestructive analysis of agri-foods: a state-of-the-art review. Trends Food Sci Technol 118, Part A:490–504. https://doi.org/10.1016/j.tifs.2021.10.010

Wu Z, Pu H, Sun DW (2021) Fingerprinting and tagging detection of mycotoxins in Agri-food products by surface-enhanced Raman spectroscopy: principles and recent applications. Trends Food Sci Technol 110:393–404. https://doi.org/10.1016/j.tifs.2021.02.013

Xiao L, Feng S, Lu X (2023) Raman spectroscopy: principles and recent applications in food safety. Adv Food Nutr Res 106:1–29. https://doi.org/10.1016/bs.afnr.2023.03.007

Xu ML, Gao Y, Han XX, Zhao B (2017) Detection of pesticide residues in food using surface-enhanced Raman spectroscopy: a review. J Agric Food Chem 65(32):6719–6726. https://doi.org/10.1021/acs.jafc.7b02504

Yang D, Ying Y (2011) Applications of Raman spectroscopy in agricultural products and food analysis: a review. Appl Spectrosc Rev 46(7):539–560. https://doi.org/10.1080/05704928.2011.593216

Zarei M, Solomatova NV, Aghaei H, Rothwell A, Wiens J, Melo L, Good TG, Shokatian S, Grant E (2023) Machine learning analysis of Raman spectra to quantify the organic constituents in complex organic–mineral mixtures. Anal Chem 95(43):15908–15916. https://doi.org/10.1021/acs.analchem.3c02348

Zhai C, Peng Y, Li Y, Chao K (2016) Extraction and identification of mixed pesticides' Raman signal and establishment of their prediction models. J Raman Spectrosc 2016. https://doi.org/10.1002/jrs.5049

Zhai W, You T, Ouyang X, Wang M (2021) Recent progress in mycotoxins detection based on surface-enhanced Raman spectroscopy. Compr Rev Food Sci Food Saf 20(1). https://doi.org/10.1111/1541-4337.12686

Zhang D, Liang P, Chen W, Tang Z, Li C, Xiao K, Jin S, Ni D, Yu Z (2021) Rapid field trace detection of pesticide residue in food based on surface-enhanced Raman spectroscopy. Microchim Acta 188(370). https://doi.org/10.1007/s00604-021-05025-3

Zhao X, Li M, Xu Z (2018) Detection of foodborne pathogens by surface enhanced Raman spectroscopy. Front Microbiol 9. https://doi.org/10.3389/fmicb.2018.01236

Zhao H, Zhan Y, Xu Z, Nduwamungu JJ, Zhou Y, Powers R, Xu C (2022) The application of machine-learning and Raman spectroscopy for the rapid detection of edible oils type and adulteration. Food Chem 373, Part B:131471. https://doi.org/10.1016/j.foodchem.2021.131471