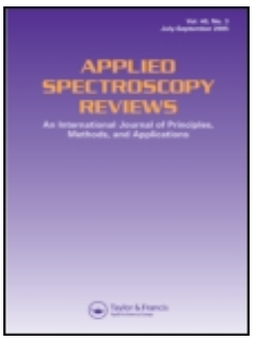

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The use of Raman spectroscopy in food processes: A review

Huaizhou Jin[a,b], Qipeng Lu[a], Xingdan Chen[a], Haiquan Ding[a], Hongzhi Gao[a], and Shangzhong Jin[c]

[a]State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin, China; [b]Department of Optics, University of Chinese Academy of Sciences, Beijing, China; [c]Department of Optical and Electronic Technology, China Jiliang University, Hangzhou, China

ABSTRACT
Raman spectroscopy is a novel method of food analysis and inspection. It is highly accurate, quick, and noninvasive. The investigation and monitoring of food processing is important because most of the foods humans eat today are processed in various ways. In this article, the use of Raman spectroscopy in food processes, such as fermentation, cooking, processed food manufacturing, and so on, are explored. The characteristics and difficulties of the Raman inspection of these processes are also discussed. According to the various research reports, Raman spectroscopy is a very powerful tool for monitoring these food processes in lab environments and is likely to see usage in situ in the future.

KEYWORDS
Raman spectroscopy; biological; organics

Introduction

Food science is a science that is involved in people's everyday lives. Humans must eat to survive and thus are looking for safe and nutritious food. Today, much of the foods humans eat are processed in some way. These processes include fermentation, heat processing, pressure processes, cooking, preservation, and so on. Even if a food item is not processed by humans, it goes through the natural process of bacterial growth, decay, and so on.

Monitoring the processes is extremely helpful and often required. For example, red wine comes from the fermentation of grapes. In order to produce high-quality wine, the process must be closely monitored. If the wine is overfermented, part of the ethanol in wine may become ethylic acid and turn the wine sour and distasteful. Sometimes, improper processing may also reduce the nutrition value of the food or introduce harmful content into the food, and such improper processing need to be avoided.

Conventional methods, such as high-performance liquid chromatography, are often used in food science to measure the contents in food (1–4). However, these conventional methods have drawbacks when used for the monitoring of food processing, because they are usually laborious,

CONTACT Qipeng Lu luqipeng@126.com State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 888 Dongnanhu Road, Erdao District, Changchun, 130033 Jilin, China.

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slow, expensive, and, most important, invasive (5, 6). On the other hand, spectral analysis methods are fast, noninvasive, and usually inexpensive and particularly suitable for food monitoring. Common spectral analysis methods include Fourier transform infrared (FTIR) or near infrared (FT-NIR), hyperspectral imaging, and Raman spectroscopy.

Raman spectroscopy is a branch of vibration spectroscopy, in which a sample is exposed to an intense light beam such as a laser, and the spectrum of Raman-active vibration modes induced in the sample molecules is obtained through analysis of the inelastically scattered photons (2).

The basic principle of Raman spectroscopy is shown in Figure 1 (7). In this process, an inelastic collision between the incident photon and the molecule of the sample occurs. As a result, the vibrational or rotational energy of the molecule is changed, and the scattered radiation is shifted to a different wavelength, and this shift is called a *Raman shift* (7). It is known that specific chemical bonds (C=C, C—H, C=O, and so on) generate specific Raman shifts, allowing Raman spectroscopy to be an effective method for probing molecular structures (8).

The diversity of applications and high content of molecular structure information provided, combined with recent advances in instrumentation, have rekindled interest in this technique in many diverse disciplines, including food science (1, 2, 7). Some key advantages of Raman spectroscopy include its speed as well as its ability to probe water-rich samples such as food items, because the peak intensities of water molecules (usually at 3000−3200 cm^{-1}) rarely overlap with the Raman peak intensities of other molecules (1, 9−11).

As a novel method for food inspection, Raman spectroscopy is not without drawbacks. First, the signal of Raman spectroscopy is quite weak; secondly, for many types of organic matter, the fluorescence is relatively strong and may overlap with the relatively weak Raman signal. Researchers use different methods to overcome these drawbacks, and these methods will be discussed in this review. Last but not the least, currently, portable or handheld Raman spectrometers are not as powerful as benchtop Raman systems; portable systems usually do not have ideal spectral detection range or spectral resolution, making the inspection of some types of samples in situ difficult (5, 12).

Fermentation

The first type of process being monitored is fermentation, most notably, the fermentation of different types of wine, especially red wine and white wine. In order to produce optimal

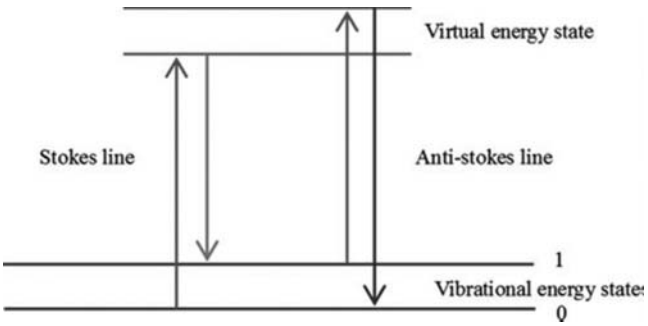

Figure 1. Energy level diagram for Raman spectroscopy.

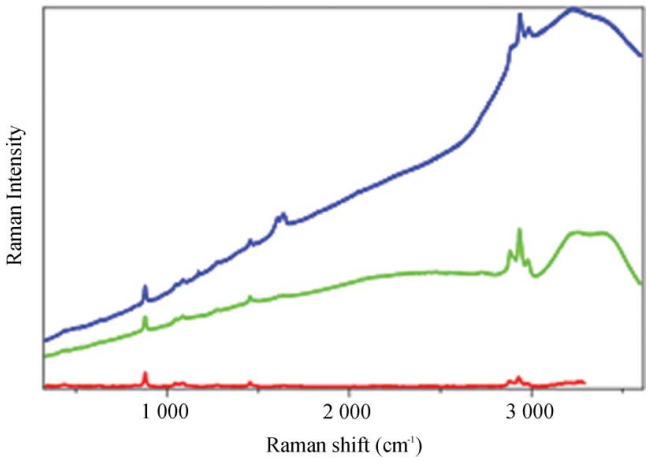

Figure 2. Flourescence in wines; blue, green, and red spectra are the same sample illuminated by 325-, 532-, and 785-nm lasers, respectively.

fermented products, the monitoring of the fermentation process is required. There are several reports on the fermentation of wine, and there are also reports on the fermentation of vinegar (from alcohol). We ourselves have also done research on fermentation of different types of plant enzymes, many of which are edible, such as Kombucha.

One of the biggest challenges researchers face during the monitoring of fermentation is the fluorescence interference from plants, as shown in Figure 2 (13). For many types of plant matter used for the fermentation of wine or enzymes, the fluorescence from plant organic compounds is strong enough that some of the Raman signals often become difficult to distinguish. The strong fluorescence can be seen in the signals of red wine, rice wine, and many plant enzymes.

There are several reports on the monitoring of fermentation using laser of even longer wavelength. Most of these reports use a 1,064-nm laser. However, silicon detectors have difficulties detecting Raman signals scattered from samples illuminated by a 1,064-nm laser due to silicon's limited spectral detection range, and InGaAs need to be used for it (14), which will make the instrumentation much more expensive. In addition, because the signal strength is inversely proportional to the fourth power of the incident wavelength, the Raman signal is much weaker than samples illuminated by a 785-nm laser or a laser with even lower wavelength, which means that using a 1,064-nm laser will require a longer sampling time. Because the goal of fermentation monitoring is often for commercial use, the cost of Raman monitoring needs to be taken into account; the longer sampling time also makes online monitoring more difficult.

Another research work used an ultraviolet incident laser (266 nm) to successfully avoid fluorescence interference in beverages with strong fluorescence such as coffee, tea, and coke (15). Figure 3 is the same sample of pumpkin seed oil illuminated by 488-nm and 266-nm lasers, and as we can see that the fluorescence is much weaker in the latter's spectrum (15). Although this report is not on fermentation or even food processing, it is worth mentioning because fluorescence interference is a difficult obstacle in the Raman monitoring of the manufacturing processes of these beverages, and methods to avoid or remove fluorescence may become useful in future research on the manufacturing processes.

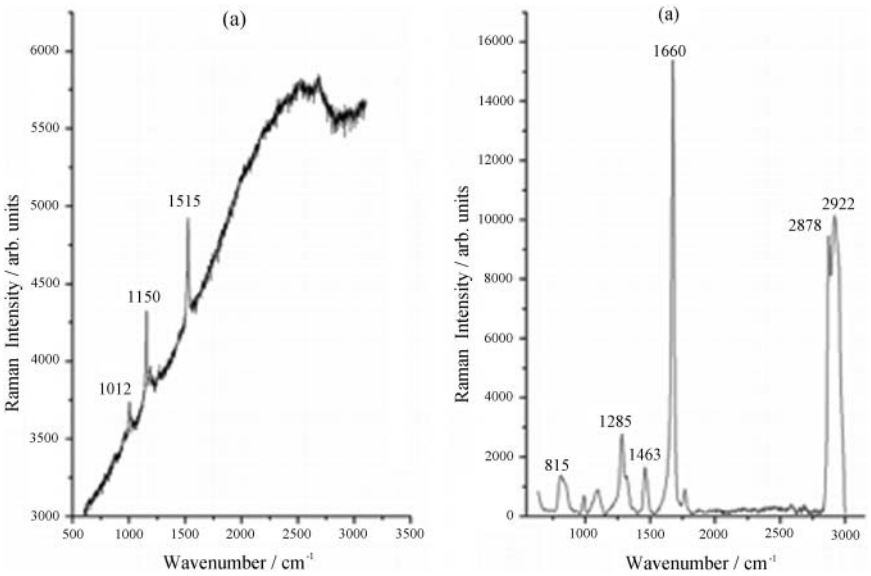

Figure 3. The same fluorescent sample illuminated by (a) 488-nm and (b) 266-nm lasers.

During fermentation of wine and some types of plant enzymes, there are two important peak intensities to look for. One is the ethanol peak at around 879 cm^{-1} (13, 15–18); the other is the ethylic acid peak at 891 cm^{-1} (17). The importance of the ethanol peak is self-explanatory; on the other hand, if the ethylic acid peak appears, it indicates that the start of the fermentation of vinegar, and measures should be taken to stop the fermentation process if the goal is to produce alcohol. These two peaks are only about 10 cm^{-1} away. This means that the spectral resolution of a Raman spectrometer is important, which is another challenge for using portable Raman systems. Currently, typical portable Raman spectrometers have spectral resolution around 6 to 10 cm^{-1}, and some systems might not be able to distinguish the two peak intensities clearly (12, 19–22).

Q. Wang et al. have successfully monitored the fermentation process on-line (16), using a 1,064-nm laser with an FT-Raman system. The spectrometer used in their research, a Bruker MultiRAM, is not a portable model (23). With the use of the FT-Raman method, the spectral resolution is also not ideal (8 cm^{-1}), but the resolution was enough to identify key components of wine, such as ethanol, sugar, and so on, in the fermentation process.

Uysal et al. reported the monitoring of the two-stage fermentation process from grape juice to wine and then from wine to vinegar (17). The fermentation of both wine and vinegar were slow; in their report, it required 90 h for the fermentation of wine and 600 h for the fermentation of vinegar. Thus, Uysal et al. did not monitor the process on-line; instead, the researchers extracted small amounts of the sample at regular intervals during the fermentation process for measurement. The report successfully shows the formation of ethanol peak intensity during the fermentation of wine and the reduction of an ethanol peak as well as the forming of acetic acid peak intensity during the fermentation of vinegar.

Chinese rice wine is also a wine with strong fluorescence interference, based on our own experiments. Z. Wu et al. (24) monitored its fermentation process.

In conclusion, Raman spectroscopy is a useful tool for fermentation monitoring; the greatest challenge that the researchers face is fluorescence. Fluorescence is an important difficulty that appears frequently in many topics probed by Raman spectroscopy. Currently, the most common way to circumvent this difficulty is to use a laser light source in relatively far ultraviolet (14) (El-Abassy et al.'s 266-nm ultraviolet laser) or infrared (16, 17) (a 1,064-nm IR laser that is more commonly used) range so that fluorescence would not overlap with Raman signals.

However, several other groups have found other ways to circumvent the fluorescence problem. In one research, a pair of laser light sources with close but different wavelengths, such as 785-nm and 801-nm, was used. Because they are similar, the fluorescence signal from the sample illuminated by both lasers would be similar, too. They then subtracted the two spectra and calculated the Raman signal (25). Though this report is worth mentioning for its potential in circumventing fluorescence interference, unfortunately we have not seen reports that use this method to eliminate the fluorescence signal in research on fermentation. This is understandable because this method requires two separate laser sources for the measurement, and if they illuminate the same spot for subtraction, the signals scattered from the two laser sources would interfere each other, which means that on-line monitoring would be extremely difficult, if not impossible.

Heating and oxidation of edible oil

Edible oil is another topic in food sciences that is frequently discussed in the modern world; many types of cooked or processed foods use oil as one of the ingredients. Raman spectroscopy has already been used on edible oil as a method for oil characterization and authentication (26–30). Most reports on Raman monitoring of the oxidation of edible oil are relatively recent.

Monitoring of the heating and oxidation of edible oil is necessary because during the heating process, the oil may become oxidized and release harmful compounds, some of which are linked to diseases such as heart disease. There are reports that monitor the heating processes of different oils and compare the oxidative damage to each oil, and the results are consistent with findings from chemical research on the heating of oils, that oils that contain more saturated fatty acids, or mono-unsaturated acids are more resistant to oxidative damage than oils that are made up primarily of poly-unsaturated fatty acids.

Though real-time monitoring of wine fermentation might have commercial use in the future, the goal of monitoring edible oil oxidation is usually more scientific in nature in the reports by various researchers. These research works might help to create guidelines for proper use of various types of edible oils.

Several research teams have monitored the heating processes of edible oil using Raman spectroscopy (26, 31–33). There are multiple peak intensities to look for, as listed in Table 1 (26–33).

Muik et al. found that olive oil contains relatively large quantities of carotenoids (26, 33), whose peak intensities (most prominent one is at 1525 cm^{-1}) decrease during the heating process, whereas the other intensities remain unchanged until the carotenoids are used up. The authors then concluded that carotenoids protect olive oil from oxidative damage,

Table 1. Peak intensities of edible oils.

Wavenumber (cm^{-1})	Chemical structure
1008	C—CH_3 bending of carotenoids
1150	C—C stretching of carotenoids
1267	Symmetric rocking of cis double bond of δ(=CH)
1302	C—H bending/twisting of the —CH_2 group
1442	δ(C—H) scissoring of —CH_2
1525	C=C stretching of carotenoids
1655	ν(C=C) cis double-bond stretching
1747	Ester stretching ν(C=O)
2850–2980	C—H stretching vibrations of methyl and methylene groups

making olive oil more resistant to oxidation than other oils made primarily of mono-unsaturated acids, such as canola oil.

Vaskova and Buckova also reported that olive oil is resistant to oxidation during heating because of carotenoids' anti-oxidative properties (31). During the heating process, the peak intensities of carotenoids decrease in intensity and the other parts of the spectrum only show changes when the carotenoids are used up, as shown in Figure 4 (31).

Because of the prominent role of carotenoids as antioxidants, we took interest in reports that target carotenoids in oil specifically. In El-Abassy et al.'s report on degradation of carotenoids (32), the researchers explored the effect of different heating methods on carotenoids in olive oil. The report shows that the degradation of carotenoids content in both microwave and conventional heating can be precisely monitored on-line using Raman spectroscopy and that a faster heating that lasts for a shorter time does less damage to carotenoids in olive oil (32).

Muik et al. (26, 33) used a 1,064-nm laser with an FT-Raman spectrometer; Vaskova and Buckova (31) used a 785-nm laser; and El-Abassy et al. (32) used a 514-nm laser. Our own experiments on oil show that for most common vegetable oils, there is no strong fluorescence interference when the sample is illuminated by a 785-nm laser. However, El-Abassy et al.'s report on fluorescent beverages (15) shows that there are several types of oil that have strong fluorescence interference, such as pumpkin seed oil.

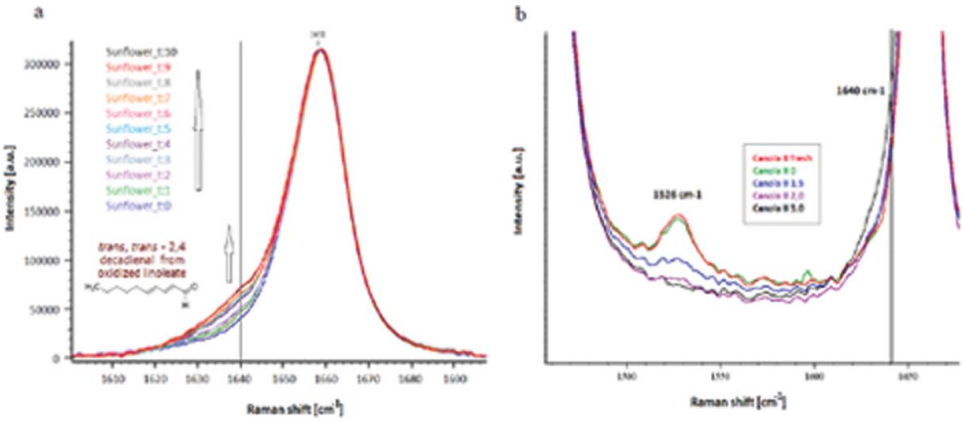

Figure 4. Thermal degradation of (a) sunflower oil and (b) olive oil, showing the influence of carotenoids.

In conclusion, Raman spectroscopy is a useful tool for the monitoring of degradation and oxidation of edible oil, and there are already examples of on-line monitoring of oil oxidation. Researchers found carotenoids to be important anti-oxidants that slow down the oxidation process and that both temperature and time are factors for oxidation; the higher the temperature and the longer the heating process, the worse the oxidation will be.

The last topic investigated in this article is meats: animal muscle, including fish muscle. There are two kinds of processes meats usually go through. Meats could be processed in a factory for ease of consumption or be stored and preserved in a freezer.

Processing and preservation of meats

Processed meats are one of the most frequently consumed types of processed foods in the world. Bacon, chicken nuggets or wings, and deli meats are all common types of processed meats consumed in the United States as well as in Europe. When meat is processed, the structure of several types of protein in meat may change, possibly resulting in a loss of nutritional value. On the other hand, during freezing, meats are stored at very low temperatures to deter bacteria growth, and this freezing mechanism may also cause structural changes and result in a loss of nutritional value.

In meats, the intensity regions of proteins and fats are worth investigating. The peak intensities of fats, or lipids, are similar to the peak intensities of fats in edible oils, as in Table 1. For proteins, the most useful Raman bands are amide I (1645−1685 cm^{-1}) and amide III bands (1200−1350 cm^{-1}), because these bands can help determine the secondary structure of protein, as shown in Figure 5 (1). However, because there are many types of specific contents in meats that researchers may choose to investigate, the exact peaks they measure vary with different reports.

One of the difficulties researchers face in the monitoring of meats is the large number of Raman peak intensities. Meats contain very complex compounds of proteins, lipids, and various other organic molecules, and the Raman intensities of these compounds often overlap with each other. Therefore, researchers often find ways to selectively enhance the signal of the compounds they need.

High-pressure treatment is an alternative to thermal treatment for meat, and it does not affect the flavor or vitamins in meat (34, 35). However, according to Wackerbarth et al., during pressure treatment, the myoglobin in meat undergoes structural changes (35). There are two natural forms of myoglobin: one is deoxy-myoglobin (deoxyMB), which is not bound to oxygen; when it binds to oxygen, it becomes oxy-myoglobin (oxyMB), which is another natural form. However, Wackerbarth et al.'s report shows that during pressure treatment, oxyMB becomes met-myoglobin (metMB), which is oxidized, ferric (Fe^{3+}) myoglobin. This structural change is undesirable for two reasons; first, metMBs causes meat to appear brown and, second, metMBs may cause oxidative damage to various other substance within meat, especially lipids, because oxidized lipids are harmful to human health.

Wackerbarth et al. conducted similar research on fish muscle and its pressure treatment (36) and showed similar findings. During pressure treatments, some oxyMBs undergo a structural change and become metMBs.

Wackerbarth et al. also suggest that because deoxyMBs do not transform into metMBs but instead transform into a nonoxidative state of ferric myoglobins, meat processers may

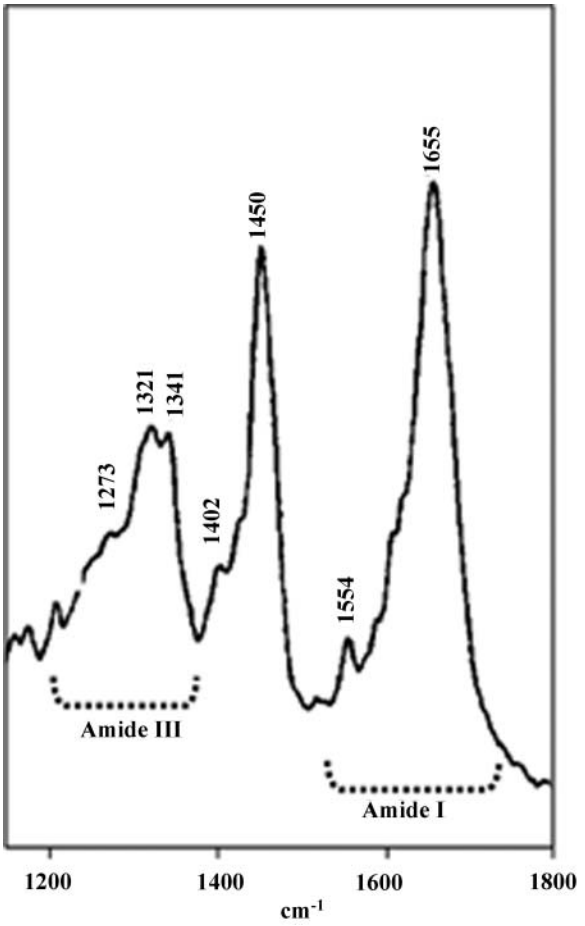

Figure 5. Key Raman intensities of protein.

find ways to keep the ratio of oxyMBs to deoxyMBs low before pressure treatment so that the process does not cause oxidative damage to other substances in meat (35).

In both reports, Wackerbarth et al. enhanced the signal of myoglobins. Myoglobins have a strong absorption band between 400 and 440 nm, and Wackerbarth et al. used a 413-nm laser in both reports to enhance their Raman signal. This form of enhancement is called resonance-enhanced Raman spectroscopy (34, 36). This enhancement method selectively enhances the signal of myoglobins, so that researchers can better examine them.

Freeze preservation is another process that meat goes through. Velioglu et al. researched the freezing and thawing of fish (37). Their discovery is that the Raman signal of the fats in fish muscle does not change much when the fish is frozen and thawed for the first time, but when fish is frozen and thawed for a second time, the Raman signal changes, implying possible nutrition loss. Because this research only studied the fats in fish muscle, fat was separated from the muscle before measurement, making the whole process invasive. Though Raman spectroscopy itself is a noninvasive method, researchers could apply

invasive pretreatments before measurement. Other researchers have used such pretreatment methods to assess meats; for example, Boyaci et al. extracted fat from meat samples to discriminate pure beef from beef adulterated with horse meat (38). However, because this pretreatment method is invasive, it is not suitable for on-line monitoring of freezing and thawing of meat.

In another report by Nache et al., Raman spectroscopy was used to monitor the metabolic parameters of pork in order to determine and predict the spoilage process (39). Nache et al. concluded that pretreatment of meat is necessary.

In conclusion, Raman spectroscopy is a relatively new method for monitoring the different processes for meat, including processing and preservation. The major difficulty that researchers face is the number of overlapping Raman signals in meat, and they need to selectively enhance the signals they need. Wackerbarth et al. used spectral resonance to successfully enhance the signal of myoglobins. Some other researchers chose to pretreat the meat and remove compounds that might interfere with the signals they need; however, pretreatment is invasive and not suitable for on-line monitoring. In order to monitor food processing for meat on-line, new, noninvasive methods to selectively enhance Raman signals need to be developed.

Discussion and conclusion

Raman spectroscopy, as a fast, noninvasive method, is a powerful tool for food process monitoring. In lab environments, monitoring on many types of processes that food items go through has been successful.

These processes include fermentation, oxidation of edible oil, and treatment and preservation of meats. In some cases, Raman spectroscopy can monitor those processes on-line; we have seen examples in the monitoring of both wine fermentation and oil oxidation.

However, because portable Raman spectrometers are not as powerful, only a few reports on successful monitoring of food processing in situ are seen. In the near future, when portable Raman spectrometers become more powerful, we may start seeing more reports on in situ monitoring of food items.

In these reports, various methods are used in the monitoring of different processes that food goes through. The important part of all these methods is that they all aim to selectively enhance the signal of the substances that are being monitored and reduce noise or interference, which is crucial to successful Raman inspection, or any spectral inspection. These reports use different methods depending on what the interference is. If the interference is fluorescence, researchers try to avoid it using a different incident laser; if the interference is Raman signal from other substances, researchers would enhance the signal of the substance being investigated, often using spectral resonance or other types of enhancement.

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