A Detailed and Systematic Study of the Applications of Raman Spectroscopy in the Agricultural Products World.

Mr.C.Kiran Kumar

Sri Vani Degree & PG College, Kakkalapalli Cross, Near Sakshi Office, Anantapuramu, Andhra Pradesh –India, 515010.

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Abstract: *This article addresses some aspects of Raman microscopy and highlights development of an instrument for Raman spectroscopy. Raman spectroscopy has become more popular, in part, because of advances in Raman specatrometry technology and the increased power of personal computers. Raman spectroscopy can detect chemical and physical information about samples without destructively analysing them and helps in analysis based on rapid on-line analysis. This article briefly discusses the application of Raman spectroscopy. Raman spectroscopic techniques are promising for various applications in agriculture, food, and/or meat products research.*

Keywords: Raman spectroscopy, surface-enhanced Raman spectroscopy, Raman spectrometry

1. Introduction

Raman spectroscopy is based on an inelastic light scattering method that was first reported by Chandrashekhara Venkata Raman and Krishnan which originates from an inelastic scattering of light known as the Raman effect. Diffusion is the essential mechanism of material waves.

1.1 Basic principles: Mechanism and Instrumentation

As a result of a process involving irradiation, a molecule will be broken apart, and in doing so will produce light in the form of "scattering" in the form of "elastic scattering". Electromagnetic scattering doesn't alter the atomic structure of photons, and no changes are made in wavelength and energy. Diffusion of light is also another form of light scattering, but diffusive diffusers like ice crystals need to be put as out. The Raman shift that results from the scattering of the Stokes scattered light by the sample is called the Dv cm. Stokes scattering is stronger than anti-Stokes scattering because of the higher pressures involved, and Raman spectroscopy is also used in food science.

2. Theoretical Basis of Raman Spectroscopy

The rays emitted by the X-ray tube are made up of photons of different wavelengths, but are clearly polarised in one direction or another. Some of those photons are absorbed by the sample. After being struck by the incident photon, the molecule makes a slight inelastic collision that allows the extra energy of the photon to be absorbed by the molecule. As a consequence of the motion of molecules and how the light is dispersed, the energy of vibrational particles is changed and the light is changed to a different wavelength. If the radio waves go between two pieces of glass, then we obtain a Raman change in the reflected radio waves. If the electron gains energy, it can be transferred to wavelengths longer than one would expect based on the classical wave-length model, or it can be shifted to shorter wavelengths where the quantized energy of the electron is captured in the electron-nucleus scattering range, such as those wavelengths where the state vector has an all-zero distribution. Figure 1 indicates the energy of the Raman scattering process occurred from 0.02 to 10 nm.

By the way, radiation waves are the way of determining the chemical composition of molecules that are the source of scattering. Fourier-transform Raman spectroscopy utilises scattered light to obtain information about molecular vibrations which can provide information about the structure, symmetry, electronic environment, and bonding of molecules; thus, Fourier-transform Raman spectroscopy's quantitative and qualitative analysis allows for the quantitative and qualitative analysis of molecules; subsequently, Fourier-transform Raman spectroscopy can also be used to provide quantitative and qualitative analyses of molecules, since concentrations of bands are proportional to the analyse concentrations, which can be explained with the following equation.

$Iv = I0KvC$ (11)

where I_v is the estimated Raman intensity, I_0 is the excitation intensity, and K_v is the constant.

And the C is the concentration of the analyte.

Raman spectroscopy has unique advantages that are important in food analysis. For example, it has high precision, strong compatibility with aqueous systems, no special sample preparation, and short timescale.

1. The Raman spectrum has a strong threshold of determination for what a sample is and is not overlapping which allows for Raman spectroscopy to be used to capture the fingerprint of samples to do the real analysis.

2. When in aqueous solutions, Raman spectroscopy has the ability to work in an atmosphere which can be excessively

dirty and noisy. It has a very good win over other spectroscopy techniques.

3. No special sample preparation is needed at all (no special sample cleaning, not even contact with the sample) and no contact with the sample is involved at all. (The Laser beam that illuminates the sample is not even applied to the sample!)

4. Fast period of time: Raman spectroscopy will complete the analysis in a few seconds. This is the spy technology of 100 years ago, easily seen on television.

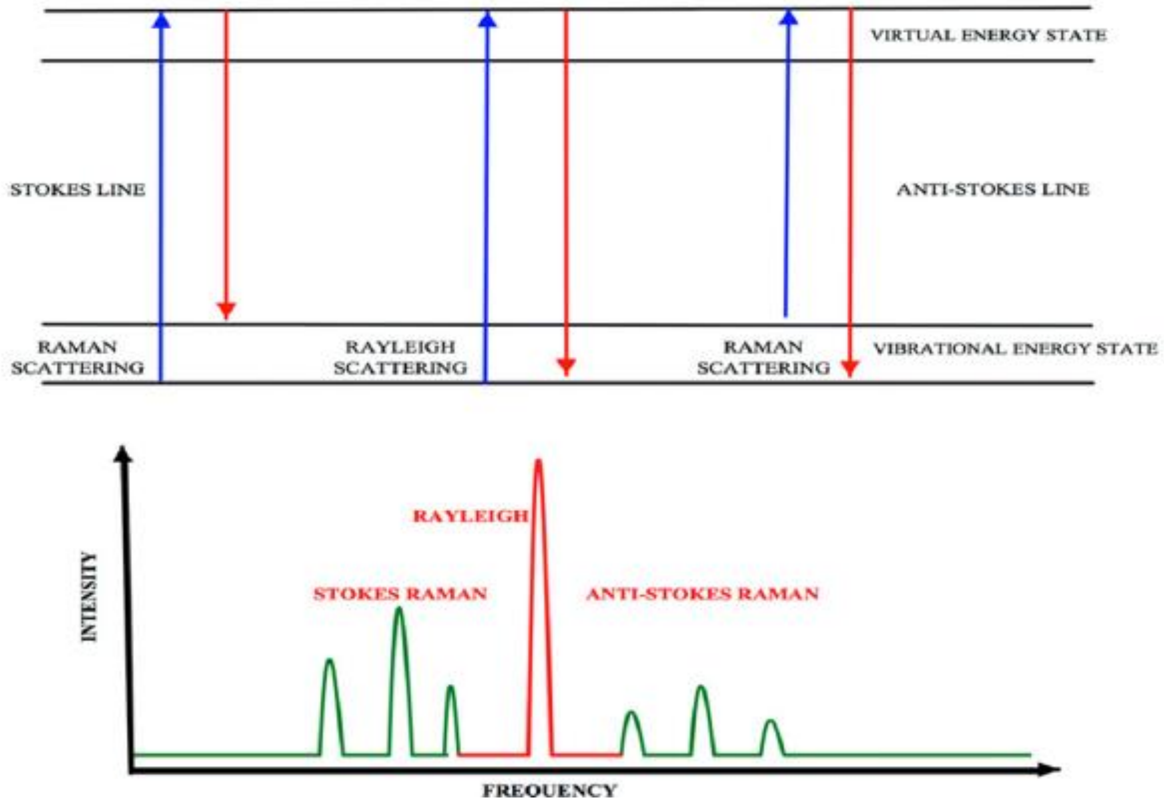

Fig.1.Energy level diagram (7-9)

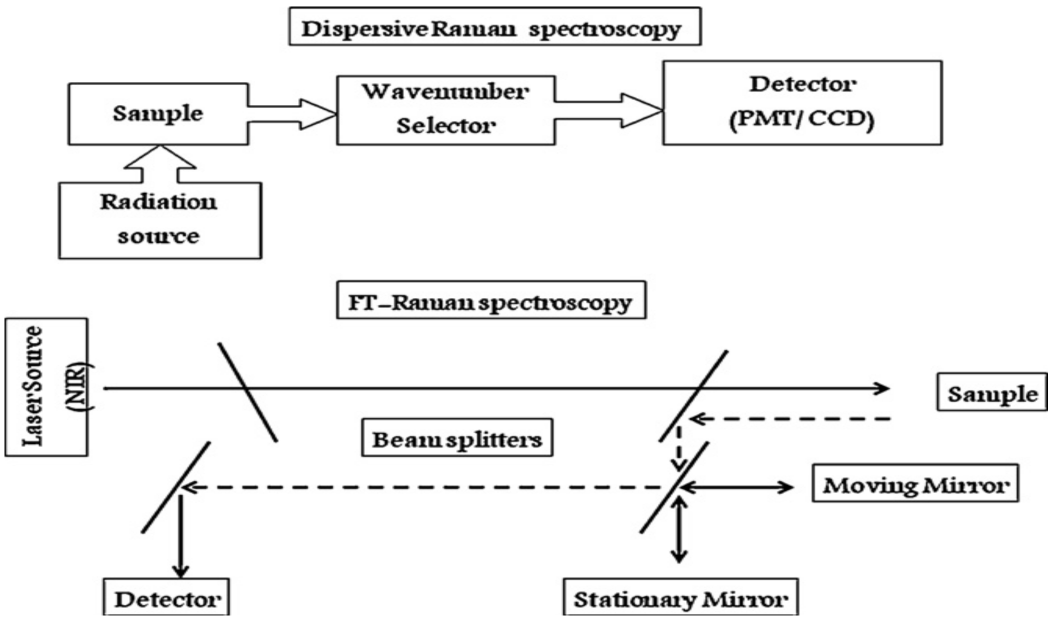

Fig.2. Instrumentation [10]

3. Raman spectroscopy Techniques:

The main Raman techniques we commonly apply in agricultural products and food analysis include dispersive Raman spectroscopy, Fourier transform Raman spectroscopy (FT-Raman), surface-enhanced Raman spectroscopy (SERS), and spatially offset Raman spectroscopy.

It needs the use of spectroscopy (SORS). A commonly used Raman spectrometer consists of four parts: a laser light source, a sampling system (instrument), a detection system (instrument), and a computer to store and record the data from the measurement. The advantages and disadvantages of the currently available optical sensors are addressed in this section. The response range of their usual equipment and the equipment appropriate for their implementation are also described in this section.

Table 1
Advantages of Raman techniques

Techniques	Advantages
Dispersive Raman spectroscopy	Is suitable for aqueous samples, samples with elevated temperature, black samples Suppresses fluorescence at 780 or 830 nm
Fourier transform Raman spectroscopy	Reduces fluorescence Eases operation with FTIR spectrometer Possesses high spectral resolution
Surface-enhanced Raman spectroscopy	Possesses high molecule specificity, sensitivity, and resolution
Spatially offset Raman spectroscopy	Has more effective illumination Suppresses fluorescence Facilitates analysis of a variety of samples

Table 2. Comparison of different optical processes.

Technique	Features	Instrumentation	Applications
Mid-IR Spectroscopy	• Absorption spectroscopy • Fundamental vibration mode • Restriction in liquid sample	• Polychromatic source, mid-IR • Interferometer, filter • IR detector	Pharmaceutical and agricultural applications, food science, microbial cells, clinical chemistry, material science
NIR Spectroscopy	• Absorption spectroscopy • Overtone and combination • Chemometrics	• Polychromatic source, NIR • Interferometer, grating • CCD, PMT	Clinical chemistry, near infrared tomography, industrial process control, water quality
Raman Spectroscopy	• Scattering spectroscopy • Fundamental vibration mode • Low intensity	• Monochromatic source, UV, visible, NIR • Grating , interferometer • CCD, PMT	Pharmaceuticals and cosmetics, geology and mineralogy, semiconductor materials characterization, life science, water quality
Fluorescence Spectroscopy	• Emission spectroscopy • Vibration mode • Presence of fluorophores	• Monochromatic source, UV • Grating, filter • PMT, APD, CCD, SPAD	Biomedical and biochemical analysis of organic samples, fluorescence lifetime imaging

CCD: charge-coupled device; PMT: photomultiplier tube; APD: avalanche photodiode; SPAD: single photon avalanche diode.

4. Agricultural Products and Food Analysis

The factors of value that are critical in the market are high quality and low costs. Furthermore, it is of great importance to maintain high internal and external quality of fruits and vegetables using quick, cost efficient analysis in modern medical and food industries. Many times researchers would use Raman spectroscopy to test the structures of fruits and vegetables to find out what the compounds are in them to be able to use it for anything to benefit society

A FT-Raman Spectroscopy study conducted by Veraverbeke et al. [16] was used to examine the natural intact wax layers on the surface of whole fruits and this study did not obtain a stable interferogram. This fact is possibly due to the high fluorescence of apple tissues. [18] [Orozco et al. 2007; Imbert et al. 2009; Prieto-Rodriguez et al. 2010] [Lopez-Casado 2005; Imbert et al. 2009; Gaspez-Murcia 2008; Hernández-Agosto et al. 2010] may be used to measure the behaviour of the individual leaflets of tomato leaves with appropriate Raman spectroscopy equipment. In their study, Synytso et al[18] demonstrated that FT-Raman spectroscopy is a very useful tool in structural analysis of commercial citrus and sugar beet pectin, and indicated that the combination of FT-Raman and FTIR spectroscopic methods offers a more complete characterization of pectin samples than either method used alone. The remarkable statistic of poets who have always been able to measure the concentrations of polyphenols calculated by Raman spectroscopy have been in good agreement with the HPLC has also been shown in the study, but the UV-Vis spectroscopy glitched an exasperating variety of 17% . Some Raman spectroscopic techniques may help account for the account of the harvest of fruits and vegetables. Using a Fourier Transform Raman Spectroscopy technique, Yang and Irudayaraj [20-22] scanned the outer surfaces of an apple for the first time. This research utilised technology like that of the comic book character thespian who uses his abilities to analyse all of the tiny parts of an apple. The visible difference, shown by an FT-Raman spectrometer, between the five different strains of Escherichia coli (E. coli) and the 100 percent accuracy of the individual species of bacteria' strains were demonstrated in my experiment; and further showed us that FT-Raman spectroscopy is an excellent tool for analysis and classification of microorganisms on food surfaces. Fortunately, there is a small portion of poor individuals who may spoil an entire crop. To know that the good from moderate-quality fruits and vegetables and the best from the most common ones is the way to maintain them at their best. A combination of metabolic profiling (in this case, LC/MS) and speciation (Raman spectroscopy) demonstrates the ability of FT-Raman spectroscopy as a technique to obtain chemical information from complex materials. Since so many different classifications exist for criteria, it is important to start by classifying Greek olives. This proposed new set of rules would not better suit the online management of process decisions, rather than the existing method of making the decisions.

4.1 Crops;

For structural and qualitative analysis of crops, Raman spectroscopy shows considerable potential to provide information about biochemical molecules within intact cells, tissues, and even plants without extraction or any other use of marking agents. The Raman spectroscopy has spread throughout the plant world, such as the cocoa plant, tobacco plant, cotton plant, rice plant, wheat plant, and so on. Cacao, also known as kakao, is the starting product that is used in chocolate processing and is a very popular drug that is used as an antiseptic, diuretic, and parasiticide. When evaluating the chemical components used in cacao, the relevance of this calculation is important to industrial value chains, even if the value chains in the sector do not include cacao. Raman spectroscopy was used in an effort to tease out and distinguish between a transgenic crop and a naturally developed crop. The research paper published in "The Tobacco Industry And Nicotine" by Stewart et al. indicated that there are significant discrepancies between transgenic and non-transgenic tobacco. In the genetically-modified tobacco, when the cinnamaldehyde (resin substance) was added into the lignin, the expression of the cinnamyl alcohol dehydrogenase (an enzyme that breaks down cinnamaldehyde) was greatly reduced. In addition, the possibility of Raman spectroscopy to distinguish between the seeds of the seed of the seeds of the varieties 'Drakkar' and the genetically modified variety 't-mix' derived from 'Drakkar' was investigated. An experiment to see the consistency of seedling grading was conducted in this way, 95.1% of the seedlings were graded correctly.

4.2 Meat and Dairy Products:

The main nutrition parameters of dietary dairy products are of great importance. To assess the value of these products, to provide their nutrition statistics, and to educate consumers about their products, you must know exactly how much of these products are consumed. Following the first assessment of fat in milk powder with Raman spectroscopy by Fehrmann et al. [35], Moros et al. [36]used an FT-Raman pectroscopy method in combination with hierarchical cluster analysis (HCA) and PLS for quantification of nutritional parameters in powdered milk and infant food formulas, such as energetic value and total carbohydrates, protein, and fat. The test results were consistent with the norm of the combined test being 3, 3, 4, and 9. The research was performed before a pre-treatment process was applied. This made the findings in the qualitative study a little more precise. McCoverin et al. [37-38] discovered the patterns that proteins and fat had a higher prevalence in skim milk powders relative to whole milk powders. It was evident from the analysis that when the derived protein content was moved in the initial protein content range, the fat content within the milk powder was found to be affected as well, which may influence the consistency of the milk powder. Raman spectroscopy has a lot of potential for investigation of meat, fish, and other food's content parameters, including protein, fat, and other nutrients. Raman spectroscopy is a method that is used to detect water soluble compounds, or reflected light, in food. The technique uses an ultrashort laser to look at individual molecules in the food. The optical Raman Spectroscopy method is also suitable for examining the structure of any form of freshwater fish because fish is not fluorescent at the 780-nm wavelengths. The Beattie et al created a spectroscopic analysis method that tests for the perceived quality of meat to provide a greater meat tenderness, meat juiciness, and its overall acceptability. There is research by which "Physicochemical investigation of different meat products by Raman spectroscopy" has proved which are the key factors influencing consumer-perceived quality, texture and tenderness.

Conclusion

Through advances in Raman spectroscopy instrumentation the spectroscopic technique of Raman spectroscopy has shown and provided new insights such as the development of potential applications. Raman spectroscopy can be a very helpful instrument to detect the condition of oceans as they occur behind the cells. This approach illustrates the extremely complex interdependence of different molecular processes within the cells. Raman spectroscopy, because of the sharp resolution, and its very narrow banding, is a perfect method for qualitative study. However, the structural knowledge tells us little about the molecule's identity.

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