

Moisture measurement in solid samples using Raman spectroscopy

Abstract. In this paper, design and experimental testing of a device for measuring moisture in the near infrared region and exploring opportunities of reflective method of measuring the solid samples, are presented. Methods with the most practical real-time usage is Raman spectroscopy, technique based on the effect that frequencies of photons in monochromatic light change after interaction with the sample induced by laser in the visible spectrum. This shift in frequency provides information about transitions in molecules, what is used in study of solids characteristics.

Streszczenie. Przedstawiono projekt i badanie eksperymentalne urządzenia do pomiaru wilgotności w obszarach bliskich podczerwieni. Zbadane zostały możliwości wykorzystania metody odbić w pomiarze próbek. Metody z najbardziej praktycznym wykorzystaniem czasu rzeczywistego oparte są na spektroskopii Ramana, technice bazującej na zmianie częstotliwości fotonów w monochromatycznym świetle po interakcji z próbkami indukowanymi przez laser w widzialnym spektrum. Zmiana częstotliwości dostarcza informacji o przejściach w molekułach używanej w badaniach ciała stałego. (Pomiar wilgotności w próbkach masywnych przy użyciu spektroskopii Ramana)

Keywords: moisture measurement, Raman spectroscopy, inelastic scattering.

Słowa kluczowe: pomiar wilgotności, spektroskopia Ramana, nieelastyczne rozproszenie

Introduction

Significant factor in agriculture is information about soil moisture. Numerous techniques have been developed to determine soil moisture, depending on the data that are needed for analysis, the cost of measuring equipment, as well as its reliability and ease of use on the terrain. Compared to conventional methods for moisture measuring based on volume and weight of water in soil unit, near-infrared (NIR) spectroscopy method has been extensively used for many agricultural applications due to its conceivable use for rapid and non-destructive determination of the concentration of certain constituents in a sample and its significant labor and cost savings [1].

Raman spectroscopy [2, 3] is a measurement technique used to provide information about vibrational, rotational and other low frequency transitions in molecules. It is based on the effect of inelastic scattering of monochromatic light induced by laser in the visible spectrum near infrared part of the spectrum. The term inelastic scattering refers to the phenomenon of frequencies change of monochromatic light photons after interaction with the sample.

Principle of Raman spectroscopy

Theory of Raman spectroscopy is based on the fact that every atom in molecules at some temperatures above absolute zero vibrates in respect to other atoms in molecules what finally means that molecule with N atoms have $3N-6$ or $3N-5$ frequency of vibrations (vibrational modes). Each of these vibrational modes provides molecules with capabilities to absorb the radiation of the same frequency because of the resonance effect.

There are two main ways to obtain values of characteristic vibration frequencies, infrared absorption spectroscopy and Raman scattering spectroscopy [4, 5]. The method of direct measurement of the characteristic frequency is based on the fact that if the sample is irradiated with infrared light, then those frequencies which correspond to the energy of the vibrational modes are absorbed. This absorption is what infrared absorption spectroscopy measures. For Raman scattering the sample is irradiated with visible light and a very small proportion is scattered inelastically. In this case the incident photon gives up a small part of its energy to a vibrational mode, and the difference between the incident and inelastically scattered radiation gives information about the energies of the

vibrational modes. Group theory and symmetry help us predict the number of the vibrational modes [6, 7] that will occur in either the infrared or Raman spectra. Therefore, both of previous explained methods are complementary and often both are needed to obtain the maximum information.

Molecular symmetry is used with group theory to predict vibrational spectra for the identification of molecular shape and point symmetry are defined as type of symmetry of a molecule located on symmetry axes and cut by planes of symmetry or centered at an inversion. Typical example of that is water molecule (Fig. 1).

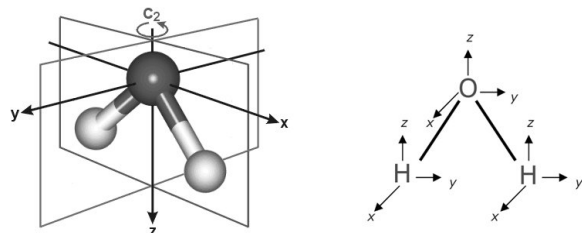


Fig.1. Symmetry operation of water molecule

Basically, for a vibrational mode to be active in the infrared there needs to be a change in dipole moment of the molecule during the vibration, and for a vibrational mode to be active in the Raman effect, there must be a change in the polarizability of the molecule during the vibration. For practical reasons prior definitions are presenting in character table (Table 1) that displacement vectors (Fig. 1) of molecule presents with numbers.

Table 1. Character table for C_{2v} point group of water

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Character tables contain, in a highly symbolic form, information about how something of interest (a bond, an orbital, etc.) is affected by the operations of a given point group. Each point group has a unique character table, which is organized into a matrix. Column headings are the symmetry operations, which are grouped into classes.

Horizontal rows are called irreducible representations of the point group. The main body consists of characters (numbers), and a section on the right side of the table provides information about vectors and atomic orbital. If the symmetry label (e.g. A_1 , B_1 , E) of a normal mode of vibration is associated with x , y , or z in the character table, then the mode is infrared active. If the symmetry label (e.g. A_1 , B_1 , E) of a normal mode of vibration is associated with a product term (x^2 , xy) in the character table, then the mode is Raman active.

The symmetry label A_1 in character table symbolize that vibration generates a changing dipole moment in the z direction, label B_1 symbolize that vibration generates a changing dipole moment in the x direction, label B_2 symbolize that vibration generates a changing dipole moment in the y direction and label A_2 symbolize that vibration does not generate a changing dipole moment in any direction (no x , y , z in the A_2 row). Thus, A_1 , B_1 and B_2 vibrations give rise to changing dipole moments and are infrared active. However, A_2 vibrations do not give rise to changing dipole moments and are infrared inactive.

From the character table emerges the irreducible representation for all the degrees of freedom within the molecule, three of which are taken up by translational and three by rotational degrees of freedom to leave three vibrational degrees of freedom. Furthermore, from Table 1 ($2A_1 + B_2$) follows that this molecule will be both infrared and Raman active. Therefore, in water there are 2 stretching modes ($\nu_1 = 3756 \text{ cm}^{-1}$, $\nu_3 = 1595 \text{ cm}^{-1}$) and one bending mode ($\nu_2 = 3652 \text{ cm}^{-1}$) as it is shown in Figure 2.

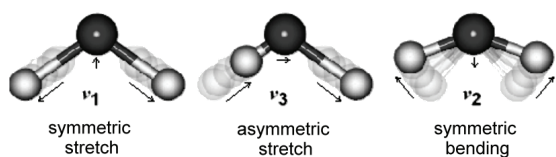


Fig.2. Vibrational modes of water

Basic theory

By definition, molecular spectroscopy deals with the response (spectrum) of molecules interacting with probing signals of known energy, and molecular vibrations can be excited via two physical mechanisms: the absorption of light quanta and the inelastic scattering of photons [6, 8]. Absorption describes the increase of molecule energy from initial (ground) state (M) to a vibrationally excited state (M') by absorption of an infrared photon energy ($h\nu_0$). Reverse process is when molecule is returned to the ground state during which emits a photon that defines infrared process.

Raman effect explains a different event; when incident photon is not to be a part of molecule during process, but only scattered from molecule. Scattering process can be elastic and inelastic when it comes to change in the energy of incident photon. Elastic or Rayleigh scattering basically describes an event when nothing changes in an interaction of photon and molecule, neither photon is absorbed, neither its energy is changed. It is the way the most photons are scattered. If the incident involves changes of photon energy as a shift in photon frequency by an amount corresponding to the energy of the particular vibrational transition then it is called inelastic or Raman scattering (Raman effect). Because of the vibrational modes of molecule energy (frequency) of scattered photon change is the opposite of molecule absorb or losses of energy (Stokes and anti-Stokes scattering as subtypes of Raman Scattering) [3]. As it is shown in Fig. 3 by thickness of lines, intensity of Rayleigh scattering is much more than Raman scattering

(around 10^7 times) which are measure for vibrational state of observed molecules. Thereby, absolutely displace of energy in Stokes and anti-Stokes scattering from Rayleigh scattering is equal because it is about the same vibrational quantum of energy, but Stokes scattering is intensive due to the fact that anti-Stokes scattering can occur only in molecules that are vibrationally excited prior irradiation.

If a shift of photon frequency as a result of Raman scattering is defined as $\Delta\nu$, according to the conservation of energy follows:

$$(1) \quad \pm h \Delta\nu = M - M' + h\nu_0 - h\nu'$$

and because the change in the kinetic energy of the molecule caused by the scattering process is negligible as compared with the total exchange of energy, it can be simplified to expression:

$$(2) \quad \pm h \Delta\nu = h(\nu_0 - \nu')$$

where $h\nu_0$ is incident photon energy before scattering process, and $h\nu'$ photon energy after scattering.

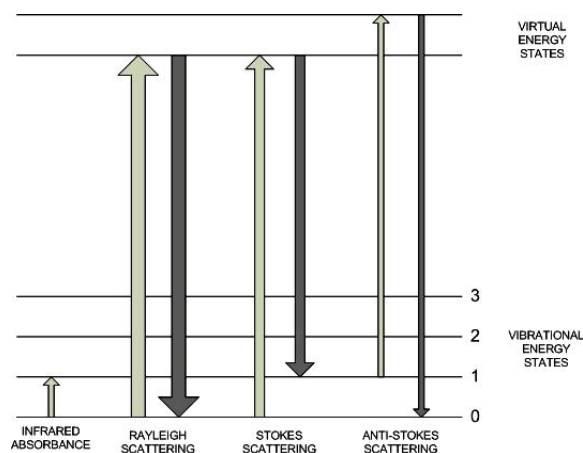


Fig.3. Energy level diagram showing the states involved in Raman signal

From (2) follow three possible results of scattering that are illustrated on Fig. 3. If the photon energy does not change, it means that molecule energy level before and after the collision are the same:

$$(3) \quad h \Delta\nu = h(\nu_0 - \nu') = 0 \rightarrow M = M'$$

and Rayleigh scattering occurs. If the photon energy of scattered light is smaller than the energy of incident photon, it means that molecule vibrational energy state increases up to the higher state,

$$(4) \quad h \Delta\nu = h(\nu_0 - \nu') > 0 \rightarrow M < M'$$

it corresponds to Stoke lines in Raman spectrum. Finally, molecule transition in lower vibrational energy state implies increase of the photon energy after collision, what corresponds to anti-Stoke lines in Raman spectrum.

$$(5) \quad h \Delta\nu = h(\nu_0 - \nu') < 0 \rightarrow M > M'$$

This shows that the frequency difference between the exciting and the scattered radiation is characteristic of a molecule and independent of the frequency of the exciting radiation.

The classical theory of Raman effect, also called the polarizability theory [9] can provide useful insights into some aspect of Raman scattering, particularly the

frequency dependence vibrational states of molecules and imposed electrical field throw incident radiation. It is known from electrostatics that the electric field \vec{E} associated with the electromagnetic radiation induces a dipole moment $\vec{\mu}$ in the molecule, given by:

$$(6) \quad \vec{\mu} = \underline{\alpha} \vec{E} = \underline{\alpha} \vec{E}_0 \cos(2\pi\nu_0 t)$$

where is \vec{E}_0 the amplitude of the vibrating electric field vector and ν_0 is the frequency of the incident radiation. With the exception of isotropic molecules the molecular polarizability $\underline{\alpha}$ shows tensor properties. The polarizability tensor will be generally a function of the molecular vibrational frequencies. Considering that the vibrations of a molecule result only in small deviations of the bonds from their equilibrium lengths, the polarizability can be expanded as a power series in the displacement r around the equilibrium value r_0 :

$$(7) \quad \underline{\alpha} = \underline{\alpha}_0 + \left(\frac{\partial \underline{\alpha}}{\partial r}\right)_{r=r_0} \cos(2\pi\nu_{\text{vib}} t)$$

From (6) and (7) by using trigonometric operation it can be derived appearing of three kinds of frequencies in expression of dipole moment in the molecule (Fig. 4):

$$(8) \quad \vec{\mu}(\nu_0), \vec{\mu}(\nu_0 - \nu_{\text{vib}}), \vec{\mu}(\nu_0 + \nu_{\text{vib}})$$

This relatively simple classical treatment provides us with a useful qualitative picture of the mechanisms of Rayleigh and Raman scattering [9]. Rayleigh scattering arises from the electric dipole oscillating at ν_0 induced in the molecule by the electric field of the incident radiation, which itself oscillates at ν_0 . On the other hand, Raman scattering arises from the electric dipoles oscillating at $(\nu_0 \pm \nu_{\text{vib}})$, which are produced when the electric dipole oscillating at ν_0 modulated by the molecule oscillating at frequency ν_{vib} .

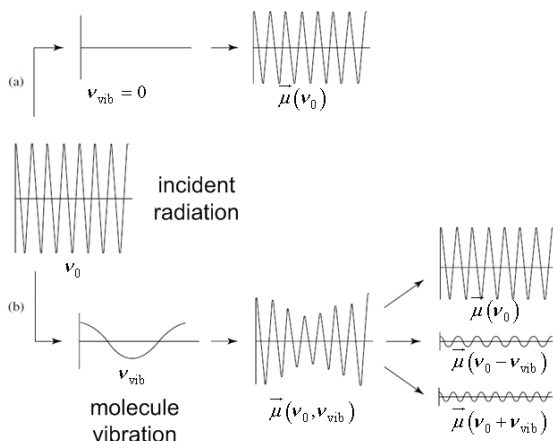


Fig.4. Time dependence of the linear induced dipoles produced by electromagnetic radiation of frequency ν_0 : (a) scattering molecule not vibrating; (b) scattering molecule vibrating with frequency

Measuring system

There are four basic components of what a typical Raman system consists. The first component is an excitation optical source. It must be strong enough to generate sufficient Raman signals and monochromatic light to provide clean and uncomplicated spectra. Because of these requirements, the most common and inexpensive gas laser, the helium-neon laser [10] is normally used in Raman spectrographs as the most suitable optical sources. The first step of Raman spectra acquisition is to set a sample of

soil in the sample chamber and to focus laser light on it with the help of a lens. Generally, liquids and solids are sampled in a Pyrex capillary tube.

The second component is a set of optics for sample illumination, on Fig. 5 presented with the steering mirror, polarizer, filter and a lens. At this stage of the scattered light from sample is collected using lens, filtered and polarized and throw final lens is focused at the entrance slit of the monochromator.

The scattered photons are collected in the third component, a double or triple monochromator [11, 12] which filters out the Rayleigh scattering, and sends the Raman signals to the spectrograph. Monochromator on exit has variable slit system by which the desired spectral resolution can be set up. The monochromator effectively rejects stray light and serves as a dispersing element for incoming radiation. The light leaving the exit slit of the monochromator is collected and focused on the surface of a detector. The spectrograph then separates the Raman signals by their wavelengths and transfers them to the light detector, which records the intensity of the accumulated photons at its own wavelength. This optical signal is converted to an electrical signal within the detector and further manipulated using detector electronics. Since the linear dispersion of the monochromator depends on the cosine of the angle of diffraction, as was previously noticed, it is impossible to achieve a reasonably constant bandpass over the wavelength range with the same grating. Instrument designers avoided this problem by using the grating in the first and the second order, depending on the wavelength investigated.

Finally, the fourth component is a signal processing system consisting of a detector, an amplifier, and an output device where these recorded data then are passed to the post processing software to display as a Raman spectrum.

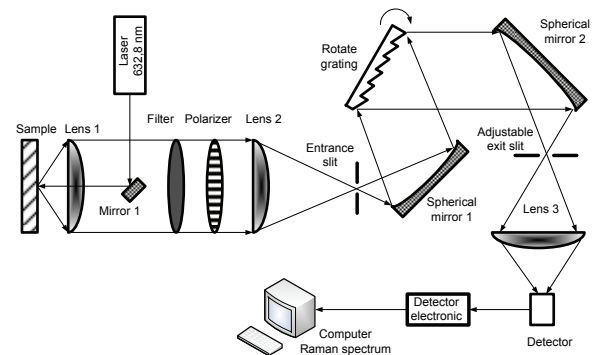


Fig.5. Schematic diagram of an dispersive Raman spectrometer using the 632,8 nm HeNe laser

Measured Raman spectrum of the soil sample (Fig. 6), furthermore, has to be compared to norm spectrum of water (Fig. 7). As it is shown on vibrational modes of water (Fig. 2), in Raman spectrum of water it is noticeable the bands of symmetric stretching ($\nu_1 = 3652 \text{ cm}^{-1}$), an asymmetric stretching ($\nu_3 = 3756 \text{ cm}^{-1}$) and a symmetric bending ($\nu_2 = 1595 \text{ cm}^{-1}$). The complete Raman spectrum of the soil sample [1] that has been tested has three bands in the region $100 \div 3500 \text{ cm}^{-1}$ (Fig. 6). Two OH bands are observed at 3355 and 3583 cm^{-1} . The band at 3355 cm^{-1} is assigned as an OH vibrational mode in their samples, which contain only 16% moisture.

Raman spectrum of wheat flour shown in Figure 8 is measured by back scattering in the reflection mode with 21% moisture. The band at 3350 cm^{-1} is most intense in the Raman spectrum and is assigned to the water OH symmetric stretching mode. The band at 3620 cm^{-1} is

assigned to the asymmetric stretching mode OH of water hydrogen bonded to water.

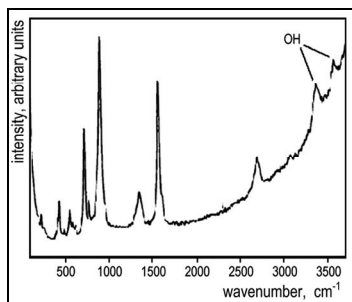


Fig.6. Raman spectrum of soil sample with 16% moisture that has been tested in the region 100–3500 cm^{-1}

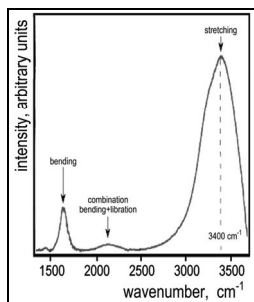


Fig.7. Infrared spectrum of water as normal spectrum

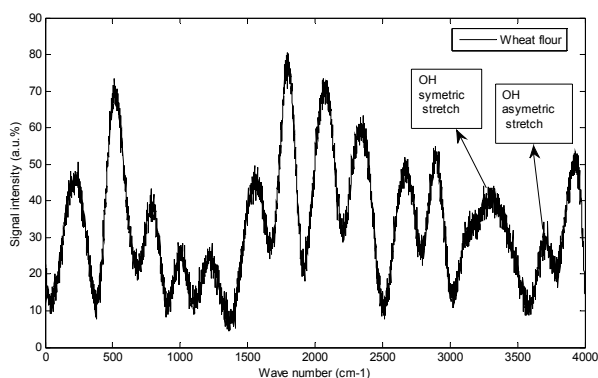


Fig.8. Raman spectrum of the wheat flour with 21% moisture

Conclusion

Raman scattering occurs because a molecular vibration can change the polarization of light. The intensity of the Raman band will be low when the polarizability derivative is near zero, what is the case if a vibration does not greatly change the polarizability. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak. An external electric field cannot induce a large change in the dipole moment and stretching or bending the bond does not change this.

Application of Raman spectroscopy to analytical chemistry is relatively new. The technique offers several potential advantages and, though it is complementary to infrared spectroscopy, it gives information that is not accessible with the latter alone. In light of this, polar bond systems with a high dipole show up strongly in IR, whereas bond systems with highly covalent character are quite easily seen in Raman. Water, as a consequence, is a weak scattered in Raman spectroscopy but strongly absorbs in IR. Therefore, water is used as a part of the sampling procedure for some of the experiments.

Because of the difference in selection rules between these two types of spectroscopic transitions, the information obtained from the two types of spectra is complementary. Another advantage of Raman spectroscopy is ease of working with heterogeneous samples. In IR spectroscopy this is difficult because of Rayleigh scatter of infrared

photons. The degree of this scatter depends on differences in the refractive indices at optical heterogeneities [13]. Due to the refractive index varies with wavelength in regions of strong IR absorption, it is difficult to separate the extinction due to molecular absorption from the extinction caused by Rayleigh scattering. For Raman spectral measurements, in contrast, discrimination against Rayleigh scattering is relatively simple.

Monitoring soil moisture levels is required mostly for effective irrigation water management. Many tried and proven methods of estimating or measuring soil moisture are available. The method selected depends on a variety of factors such as accuracy, cost, and ease of use. In opposite to those classical methods of monitoring soil moisture, the best advantage of Raman spectroscopy is real time measurement that gives digital spectrum which is easy to process and convert in any suitable format and the best example of that is newest lunar exploration.

REFERENCES

- [1] Lee W. S., Sanchez J. F., Mylavarapu R. S., Choe J.S., Estimating Chemical properties of Florida soils using spectral reflectance, Agricultural and Biological Engineering Department University of Florida, Gainesville, Florida, *Trans. ASAE*, 46(5), (2003.), 1443-1453
- [2] Rossman, G. R. Vibrational spectroscopy of hydrous components, *Reviews in Mineralogy and Geochemistry*, 18(1), (1988), 193-206
- [3] Barrow G. M. Molecular Spectroscopy, *McGraw-Hill International Book Company*, New York (1962)
- [4] Long D. A., Raman Spectrometry, *McGraw-Hill International Book Company*, London, (1977)
- [5] Banwell C. N., McCash E. M., Fundaments of Molecular Spectroscopy, *McGraw-Hill International Book Company*, London (1994)
- [6] Herzberg G., Molecular Spectra and Molecular Structure, Vol. II: Infrared and Raman Spectra of Polyatomic Molecules, *D. Van Nostrand Co. Inc.*, (1945)
- [7] Diem M., Introduction to modern vibrational spectroscopy, *John Wiley & sons*, New York (1993)
- [8] Svanberg S., Atomic and molecular spectroscopy – Basic aspects and practical applications, *Springer Verlag*, Heidelberg (2004)
- [9] Long D. A., The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules, *Copyright © 2002 John Wiley & Sons Ltd*, ISBN (0-471-49028-8)
- [10] Corney A., Atomic and Laser Spectroscopy, *Oxford University Press*, Oxford (1977)
- [11] Harrison G.R., Loewen E.G., Wiley R.S., Echelle gratings: their testing and improvement, *Applied Optics*, 15(1976), 971-976
- [12] Shurcliff W.A. Polarized Light, *Harvard University Press*, Cambridge (1966).
- [13] Kerker M., *The Scattering of Light and Other Electromagnetic Radiation*, *Academic Press*, New York (1969)

Authors: mr.sc. Venco Čorluka, Josip Juraj Strossmayer University of Osijek, Faculty of Electrical Engineering, Kneza Trpimira 2B, 31000 Osijek, Croatia, E-mail: venco.corluka@etfos.hr; doc.dr.sc. Željko Hederić, Josip Juraj Strossmayer University of Osijek, Faculty of Electrical Engineering, Kneza Trpimira 2B, 31000 Osijek, Croatia, E-mail: zeljko.hederic@etfos.hr; doc.dr.sc. Miralem Hadžiselimović, University of Maribor, Faculty of Energy Technology, Hočevarjev trg 1, SI-8270 Krško, Slovenia, E-mail: miralem.h@uni-mb.si