Raman spectroscopy as an innovative method for material identification

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Abstract: - Raman spectroscopy has become a powerful analytical and research tool with assertion in almost all sciences and a wide range of technical and industrial branches. Although the fundamental principle of this method is known almost one hundred years, extensive potentialities which Raman spectroscopy offers are finally able due to a technical advancement and novel engineering solution of the last two decades. This technique is one of the most essential laser spectroscopic methods. This paper introduces the basic principle, advantages and disadvantages and demonstrates great applicability of Raman spectroscopy. Others currently examined applications are also presented.

Key-Words: - Raman spectroscopy, spectrum, identification, fluorescence, material properties.

1 Introduction

Laser spectroscopic research yields essential knowledge necessary for the insight into the world of atoms and molecules dimensions. Especially Raman spectroscopy is a powerful analytic method providing detailed and specific information on a molecular level. In regard of its versatility this method can offer information that can be below possibilities of other spectroscopic methods [1].

Raman effect was discovered almost one hundred years ago. However, renaissance of Raman spectroscopy is coming even in the last two decades hand in hand with technical advancements as are new extremely sensitive detection devices latest developments, efficient filters and laser technology designs [2].

The fact, that Raman spectroscopy is a very flexible method in majority of science and technical branches, has been repeatedly proven during the last few decades.

A structure and a composition of materials influence their physical utility properties and consequently characteristics of products fabricated from these materials. In many cases strict and specific conditions that must be complied are given. Critical properties on the possibility borders of examination must be attested. Raman spectroscopy is a powerful tool for such verification within a wide range of scientific disciplines. This rapid method allows quick identification of materials, gives information on the structure, spatial arrangement of molecules and structural analyses. Analogically to the reality that every human being in the world has different – unique – set of fingerprints by which can be identified, also every individual substance has its own unique Raman spectrum characteristic only for the respective substance. Raman spectroscopy also enables observation of the structural changes dynamics, mapping, depth scanning and with Infrared spectroscopy is a complementary spectroscopic method.

2 Theoretical background

Raman scattering, the fundamental principle of Raman spectroscopy and the whole technique are named in honour of one of its discoverers, the Indian scientist Sir Chandrasekhara Venkata Raman (1888 - 1970), who searched out the effect in 1928.

Raman effect occurs when a monochromatic light is shone on a researched material. A major part of light beam usually from near infrared, visible or near ultraviolet range is scattered without changes in frequency, i. e. Rayleigh (elastic) scattering, a part is absorbed and a remained tiny fraction, important for origin of the spectra, is non-elastically scattered. After interaction of the photon with the molecule, particularly with the electron cloud and the bonds of the molecule, the photon evokes molecule excitation from the ground state to a virtual energy state. When

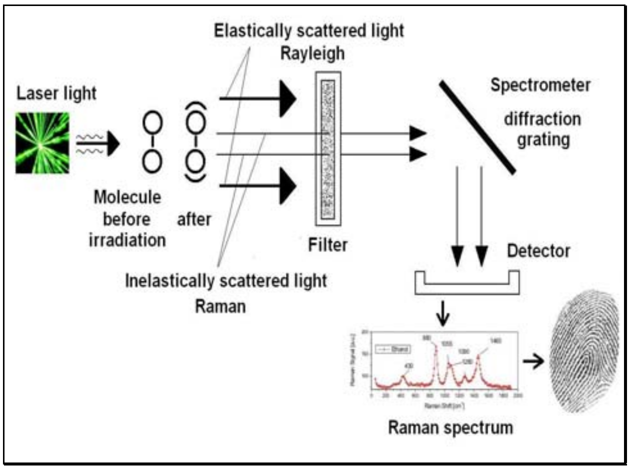

Fig. 1. The sample is irradiated with laser, molecule vibrato, filter eliminates intense Rayleigh scattering, the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding.

the molecule relaxes it emits a photon and it returns to a different vibrational or rotational state. The energetic difference, between the ground state and the final state, results in a shift in the emitted photon's wavelength.

If the molecule absorbs energy, i.e. the final state is more energetic than the initial state then the emitted photon of a higher wavelength generates a Stokes line. If the molecule loses energy, the emitted photon of a lower wavelength generates an anti-Stokes line. These wavelength shifts carry analytical information on differences between the individual quantum levels and play the key role in substance identification.

Mostly only a more intensive (Stokes) part of the spectrum is measured. Both Stokes and anti-Stokes are approximately symmetrical towards the zero shift of the wavelength that corresponds with the incident laser line wavelength. Distribution of the lines in the spectrum informs about a sort of the bonds in the molecule. Every individual substance has its own unique Raman spectrum characteristic only for the respective substance.

Raman spectrum represents a dependence of intensity of the scattered light on wavelength (measured in nm) or a Raman frequency shift (measured in cm^{-1}). Intensity of the Raman scattering depends on several factors as the excitation wavelength of the used laser, used excitation power, changes in polarizability, the amount of Raman active molecules illuminated by the laser beam and temperature. The intensity of a Raman-band is theoretically described by George Placzek [3].

In spite of the fact, that the particularity of Raman spectroscopy is remarkable, the conversion efficiency of Raman effect is rather poor, since only a scarcity (about 10^{-7}) of the initial photons are non-elastically scattered. Hence the detection of very low concentrated molecules is limited.

In order to enhance sensitivity, to improve intensity, to reach better spatial resolution and other improvements number of variation of RS has been developed: Surface Enhanced RS, Resonance RS, Transmission RS, Spontaneous RS, Tip-Enhanced RS et al.

2.1 Advantages of Raman spectroscopy

Raman spectroscopy has a number of indisputable advantages which appreciate scientist form variety spheres. The method is:

- Non-destructive – after Raman analyse can be sample consequently treated by other procedures.
- Non-contact - no contamination of a sample happen, it is convenience for e. g. toxic substances which can be measured through protective or covering layers or packages from other materials as glass or plastics. Spectra of these packages can be later subtracted using the software designed for another manipulation with data.
- Requiring no need for sample preparation in most cases - that is convenient and prompt.
- Highly sensitive - high spatial resolution in the order of µm. Currently the most commonly used Raman spectrometers are combined with microscopes. Then only a very small volume (about ones of µm in diameter) of a sample is needed for collecting Raman spectra when using Raman microscopy. This interconnection yields many benefits.
- A rapid method – Raman spectra are acquired within seconds (e. g. chemical analyses generally take minutes or even hours).
- Applicable to a wide range of substances as liquids, transparent solids, gases; organic and inorganic compounds as well.
- Providing possibility of aqueous solutions exploration since water does not generally interfere with Raman spectral analysis.
- Granting highly specific chemical "fingerprint".

The intensity of spectral features is directly proportional to the particular species concentration. The standard spectral range ideal for both organic and inorganic samples covers from 100 cm^{-1} to 3200 cm^{-1}.

2.2 Disadvantages of Raman spectroscopy

In spite of many advantages a well known competing process can appear along with the Raman scattering: fluorescence. Raman spectra, for instance, of certain biological samples are often overlaid by fluorescence when visible wavelengths of laser are used. A solution often consists in a selection of suitable laser wavelengths preferably with lower photon energy. Thereby spectrometers equipped by several lasers with different excitation wavelengths are recommended to overcome the problem with fluorescence [4]. The interfering luminescence background can be also in some cases reduced by so called “bleaching”, i.e. prolonged sample illumination with the laser beam antecedent to concrete measurement [5].

3 Applications

Raman spectroscopy finds application in many scientific and industrial disciplines and branches such as:

- Material sciences – Raman spectroscopy is one of the best-known methods, it is of central importance for all the specification and structural analysis of almost all kinds of materials (amorphous, partially crystallic, transparent, non-transparent samples, samples with different surface textures).
- Chemistry – Raman spectroscopy provides a chemical fingerprint for identification of a molecule, since vibrational information is specific to the chemical bonds and symmetry of molecules.
- Forensic sciences – Raman spectroscopy is becoming a tool of major importance in forensics science due to a mentioned advantages above all that it is a non-destructive, non-contact method without the necessity of sample preparation. Method is used for identification of trace amounts of substances in evidential materials, etc. In-situ measurements can be realized, meaning no contamination of evidences during taking samples [4].
- Criminology, security forces – identification of unknown or hazardous substances, by instance detection of explosives or drugs by airport security can be realized via portable spectrometers, etc.
- Medicine and biology – applications benefiting Raman spectroscopy involve e. g. DNA analyses, prognoses and diagnoses of carcinomas, study of biological systems, etc.
- Pharmaceutical industry – the role that Raman spectroscopy plays in Pharmaceutical research, development, manufacturing and control of active substances of pharmaceuticals (even through packing) is still rising.
- Nanotechnology – Raman spectroscopy provides determination of nanocrystals, chirality, semidiameters in nanomaterials.
- Semiconductor industry – Raman spectroscopy allows semiconductor impurities determination in silicone substrates and diamond-like carbon coatings (a point measurement on silicone can be obtained in about 0.1 second), identification of defects particles on the material surfaces. Such results notably affect device yields and the economics of the process line.
- Solid state physics – materials characterization, finding the crystallographic orientation, etc.
- Geology and mineralogy – Raman spectroscopy serves for identification of the principal mineral phases or classification of rocks, etc.
- Art – (micro) Raman examination of artworks and artefacts reveal worthy information for conservators or those of general historical interest.

Followed issues are solved at the present time using Renishaw inVia Basis Raman microscope with the 514 nm excitation Argon ion laser at Faculty of Applied Informatics, Tomas Bata University in Zlin. The methodology for the detection of small Cr(VI) concentrations with the use of Raman spectroscopy is developed. Trivalent and hexavalent chromium compounds are produced in large quantities and are accessible to most of the population. However, Cr(VI) is a carcinogenic substance and may cause health risks. There is a possibility of conversion of Cr (III) into Cr (VI). It is already proved that Raman spectroscopy can distinguish Cr (III) from Cr (VI) [6] (Fig. 2). Obtained results showed the complication with fluorescence that masks the Raman spectra of natural polymers containing

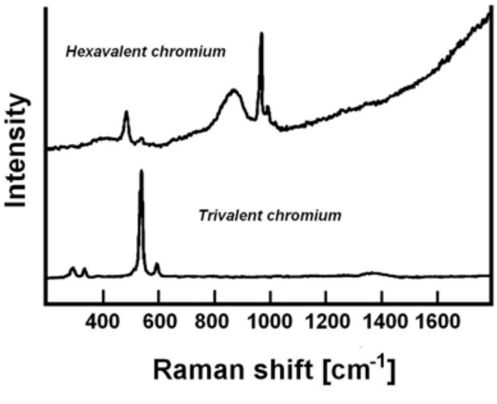

Fig. 2. Raman spectrum of Cr(III) and Cr (VI)

chromium compounds. This situation has been so far solved by shortening the exposure time to tenths of seconds.

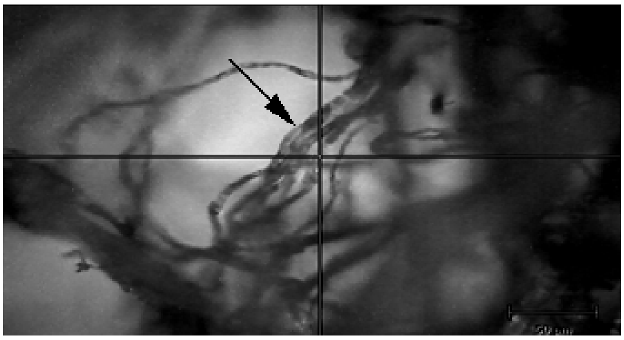

Fig. 3. Fibres of leather with linked Cr(VI)

Raman spectroscopy has been also used for monitoring the curing process of epoxy resins. Due to a time series measurement can the kinetics of crosslinking be controlled and the changes in active chemical groups and bonds recorded and analysed.

Application of Multi-Walled Carbon Nanotube (MWCNT) for the purpose of conducting layers creation is investigated. Raman spectroscopy is very useful in the detection of carbon form in fundamental research and also in industrial usage. This technique is able to distinguish different forms of carbon (Fig.4.), because of evident Raman spectral variances, and also map them. While, for example, SEM indicates only presence of elemental carbon in the sample [2]. Different concentrations of MWCNT affect properties of electric conductivity of layers, which are used for shielding electromagnetic fields or elimination of static charge and others.

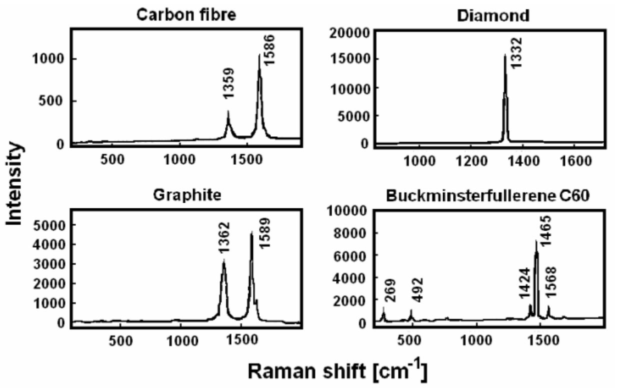

Fig. 4. Raman spectra of different modifications of carbon

Other applications of this potential method as identification of cadmium sulphide nanoparticles or determination of inks within the scope of security usage are upcoming issues at present time.

4 Conclusion

Raman spectroscopy is rapidly progressing method. Raman (micro) spectrometers are becoming essential and unnecessary equipments for researchers in variously specialized laboratory such as forensics, pharmaceutical, laboratories for development of nanomaterials or laboratories focused on examination of artworks.

Raman spectroscopic technique was studied as an innovative method for obtaining information about a structure and properties of a wide range of materials, which can be used in almost all technical and industrial branches. Measurements on a concrete device InVia Basis Raman Microscope were realized. Possibilities of both a structure and properties of selected materials were verified. Laboratory program for forensic applications, mechanical properties and aging of solids is preparing at the present time.

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