

A powerful tool for material identification: Raman spectroscopy

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Abstract—In present time different analytical methods with specific limitations serves for material identification. Raman spectroscopy is one of the most essential laser spectroscopic methods. In principle, Raman spectroscopy has the potential to answer a number of questions pertaining to chemical details of molecular structure what makes this technique definitely proper for material identification. Raman spectroscopy has recently proved progressive benefits and become a powerful research tool which finds assertion in almost all sciences and a wide range of technical and industrial branches. Doubtless advantages as non-destructiveness, contactless measurements, rapidity or no demand for sample preparation makes Raman spectroscopy attractive, convenient and effective. In the light of these facts, the popularity of Raman spectroscopy is still growing in analytical laboratories all over the world. 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 recent years. This paper briefly introduces the principle of the method, highlights its advantages, discusses drawbacks and compares its possibilities with infrared spectroscopy. Great applicability of Raman spectroscopy is demonstrated in the paper, other currently examined applications as determination of carcinogenic hexavalent chromium or epoxy resin crosslinking monitoring are also presented.

Keywords— Fluorescence, identification, material properties, Raman spectroscopy, spectra.

I. 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 at a molecular level. In regard of its versatility this method can offer information that can be below possibilities of other spectroscopic methods [1]. From a general point of view an interaction of electromagnetic radiation with a matter, particularly a specific emission and absorption of light, provides essential and valuable acquaintances of chemical agents.

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Raman effect was discovered more than eighty years ago. For a long time it remained only on a theoretical level and practically was marginalized because of low sensitivity and difficulties with overcoming fluorescence phenomena. 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 for filtering Raman scattered light from the Rayleigh scattering and introducing lasers as light sources and also innovative laser technology designs [2].

The fact, that Raman spectroscopy is very flexible method in majority of sciences and technical branches, has been repeatedly proven during recent years, when problems from different scientific areas have been solved.

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 technique 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. Except material identification Raman spectroscopy also enables observation of the structural changes dynamics, mapping of samples and depth scanning.

With regard to Raman molecular structure fingerprint this analytical method is suitable particularly for qualitative analyses, but can be also used for quantification, because the intensity of Raman scattered light is related to the amount of particular substance in a sample. Quantitative studies require often non-linear calibrations and standardization of the Raman signal. When doing quantitative analyses it is crucial to have as stable instrument as is possible, to assure measurement parameters identity as are laser power, time of irradiation, spectral resolution, number of acquisitions or sample orientation and also consider data post-processing. Obviously doing quantitative analyses of liquids and (water) solutions is better and more proper than analyses of solids because of their bigger homogeneity.

II. RAMAN AND INFRARED SPECTROSCOPY

Raman spectroscopy and infrared spectroscopy are advertised as complementary techniques. Both methods provide information about vibrational and rotational transitions in molecule and serve as a good tool for material identification even though principles of these methods are different. However, Raman spectroscopy is not so popular for the chemical analysis of materials as is infrared spectroscopy.

Infrared spectroscopy is an absorption technique dealing with the fact that molecules absorb specific frequencies that define their structure. The output data are absorption spectra. On the other hand Raman spectroscopy provides emission spectra originated during interaction of the monochromatic excitation laser beam with molecules, which emit on for the matter characteristic frequencies. This elemental difference is shown in Fig. 1.

IR spectroscopy x Raman spectroscopy

Absorption



Raman scattering



Fig. 1 Differences of light-matter interaction of infrared and Raman spectroscopy

Certain substances have high-quality both Raman and IR features, but for instance centrosymmetric molecules modes give a rise either Raman or infrared spectra but not both. Strong infrared absorptions usually appear as weak Raman signal and vice versa. Infrared spectroscopy has more intensive signal for small polar molecules and single bonded chemical compounds like C-C, C-O, C-H etc. Large absorption bands of water caused by containment of high absorptivity values functional groups disallow infrared measurement of water solutions. On the contrary presence of water in a sample can be determined with ease. Intensive spectra of polyatomic inorganic chemical compounds and majority of organic matters yields Raman spectroscopy. Raman spectrum of water is minimal thereby substances dissolved in water can be identified without problems. A demonstration of infrared and Raman spectrum of styrene-butadiene rubber can be seen in Fig. 2.

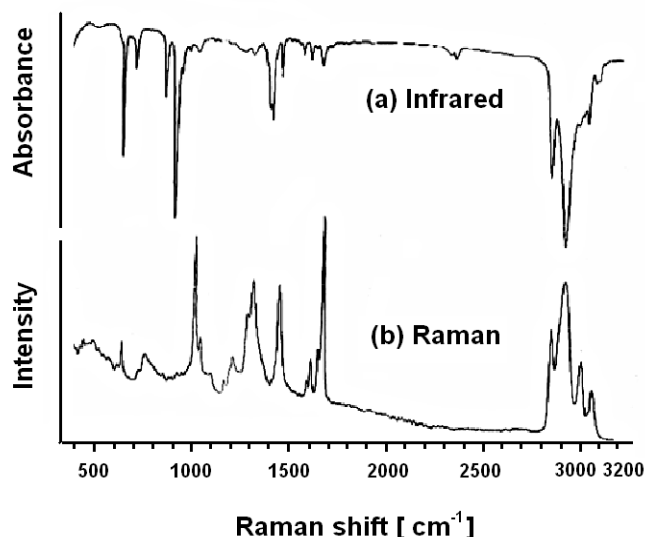


Fig.2 Infrared and Raman spectrum of styrene-butadiene rubber

From time to time a complication with other quantum process fluorescence, which occurs with a time delay, can appear and disrupt acquiring of Raman spectra.

III. 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 together with Kariamanikkam Srinivasa Krishnan (1889 - 1961) in 1928. Sir C. V. Raman was awarded a Nobel Prize in physics in 1930 for the discovery of the effect and his work on the scattering of light.



Fig.3 Sir C. V. Raman and Sir K. S. Krishnan

As is known, molecules have an ability to absorb or emit photons – an electromagnetic radiation with specific energy and by that change their own energy. According to the quantum theory the energy of a photon E is given by the equation:

$$E = h\nu \quad (1)$$

or

$$E = hc\bar{\nu} \quad (2)$$

where h is Planck's constant, ν is its frequency, $\bar{\nu}$ is the wavenumber, thus the reciprocal wavelength. Mentioned specific energy ΔE have to fulfill following quantum condition

$$\Delta E = |E_p - E_q| = h\nu = \frac{hc}{\lambda} \quad (3)$$

E_p and E_q are energies of different quantum states in which a molecule can exist, c is the velocity of light and λ is the wavelength. So the energy of a molecule will be changed by an amount E , if the molecule absorbs or emits the photon.

Raman effect occurs when a researched material is irradiated by an intense monochromatic light. A major part of light beam usually from near infrared, visible or near ultraviolet range is scattered without changes in frequency, no energy is gained or lost, i. e. Rayleigh (elastic) scattering, a part is absorbed and a remained tiny fraction, important for the 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 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. Energy level diagram illustrates Fig. 4. The schematic principle of the Raman spectroscopy is shown in Fig. 5.

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

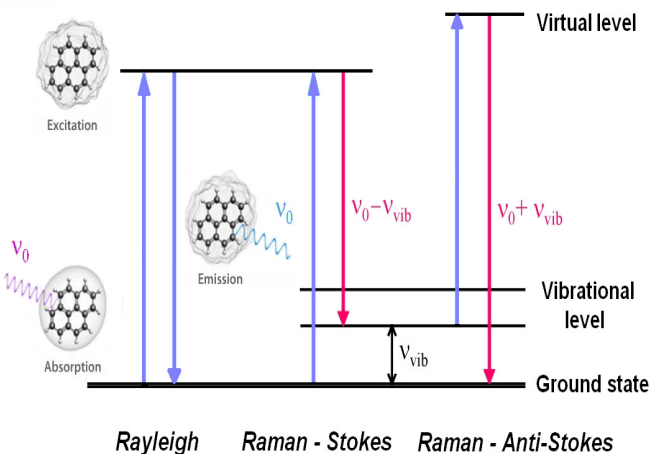


Fig.4 Energy level diagram of Rayleigh and Raman scattering

Raman shifts depend on the specific molecular geometry of the material and are independent on the incident photon wavelength, i.e. on the excitation wavelength of the laser [3]. There can exist several characteristic shifts for certain material which originates the Raman spectrum.

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 (in arbitrary units) on wavelength or on 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 [4].

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 Raman spectroscopy has been developed: Surface Enhanced RS, Resonance RS, Transmission RS, Spontaneous RS, Tip-Enhanced RS et al.

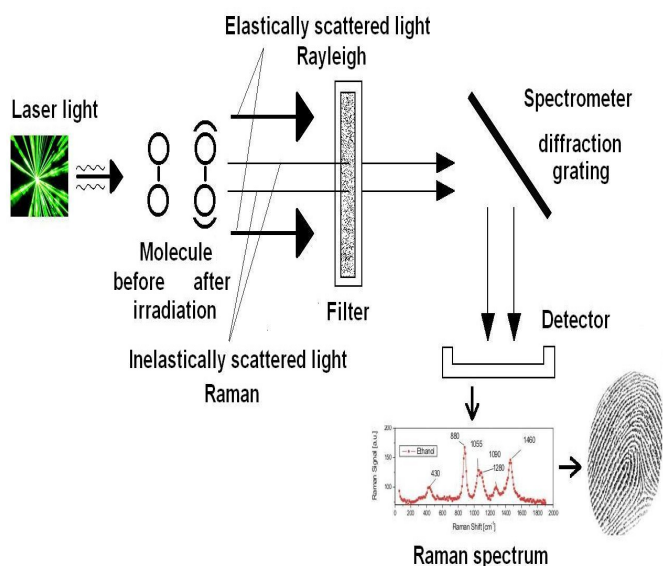


Fig. 5 The sample is irradiated with laser, molecule vibrates, filter eliminates intense Rayleigh scattering, the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding and provides a chemical fingerprint utilizable for identification.

IV. ADVANTAGES AND DISADVANTAGES OF RAMAN SPECTROSCOPY

A. Advantages of the method

Raman spectroscopy has a number of indisputable advantages which appreciate scientist from variety spheres. These benefits go towards the growth of popularity of Raman spectroscopy in laboratories worldwide. The method is:

- Non-destructive. Sample can be after Raman analysis consequently treated by other procedures. Non-destructiveness also enables potential as in-vivo diagnostic tool in medicine providing information about both the chemical and morphologic structure of tissue in quasi-real time.
- Non-contact. No contamination of a sample happens. This is convenience and safe. For example dangerous and toxic samples or those with unpleasant smell, substances with unknown composition, properties, and history from the scene of an accident, samples, that are unstable to air or moisture can be measured through protective or covering layers or packages from other materials as glass or polymers. Spectra of these packages can be later subtracted using the software designed for manipulation with data. Raman spectroscopy therefore appears as an easy and strikingly useful technique analyzing and identification of materials even in packing.
- No need for sample preparation prior the analysis is required - that is convenient and prompt. No physical or chemical conditioning of sample (diluting, pressing into pellets, etc.) is necessary.
- Highly sensitive. High spatial resolution is in the order of micrometers. Currently the most commonly used Raman spectrometers are combined with microscopes. Then only 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 e. g. for forensic science investigation of trace amounts of evidences.
- A rapid method. High quality Raman data are acquired in very short periods of time, often within seconds. E. g. chemical analyses generally take minutes or even hours. This kind of analysis definitely spares time. The rapidity of the method yields further potentialities inherent in a scope of almost immediate response and quasi real time processes e. g. chemical changes kinetics monitoring.
- Applicable to a wide range of substances. Via Raman spectroscopy is possible to measure liquids, transparent solids and gases. Samples can be in a form of powder, crystal set, fiber, thin layer, gel, solution, etc. with no concern with sample size, shape or thickness. The method is also appropriate for analyses of organic and inorganic compounds.
- Providing possibility of aqueous solutions exploration since water is very weak Raman scatterer and generally almost does not interfere with Raman spectral analysis. This is a great advantage in comparison with infrared spectroscopy where the presence of water or moisture is unfavourable.

- Granting highly specific chemical “fingerprint”. Each compound gives rise to a unique Raman spectrum.
- The standard spectral range ideal for both organic and inorganic samples covers from 100 cm^{-1} to 3200 cm^{-1} and can be covered by a single spectra recording.
- The intensity of spectral features is directly proportional to the particular species concentration.
- Remote analyses can be realized. Transmission of laser light and Raman scattered signal can be done by fibre-optic probes over long distances – up to hundreds of meters far from the base of Raman analyzer.

B. Drawbacks of Raman spectroscopy

As with all problems we solve and take into account related advantages, we have to consider either the weak side - limitations. In spite of many advantages of Raman spectroscopy a well known competing process can appear along with the Raman scattering: fluorescence. Fluorescence signal is generated by a part of matter that undergoes an electronic transition to an excited state what initiate emission of light at a wavelength which is changed from the excitation laser. A mechanism controlling both effects is similar and determines that if one of the phenomena occurs, the second will likely as well. Fluorescence initiation probability versus probability of Raman scattering initiation is in the order of 1 photon in 10^3 - 10^5 versus 1 photon in $10^6 - 10^9$. Hence we always have to consider fluorescence interference. Raman spectra, for instance, of certain biological samples are often overlaid by fluorescence when visible wavelengths of laser are used. There exists ways to avoid or at least minimize this adverse effect A solution often consists in a selection of suitable laser wavelengths preferably with lower photon energy. As the laser excitation wavelength gets shorter the Raman scattering intensity increases but fluorescence tends to be less troublesome as the laser wavelength gets longer [5]. Thereby spectrometers equipped by several lasers with different excitation wavelengths are recommended to overcome the problem with fluorescence [6]. 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 [7].

Even though Raman spectroscopy can be applied on measuring an extend spectrum of materials, metals and alloys are not Raman active.

Other disadvantage of Raman spectroscopy is the sensitivity of the method. 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^{-6}) of initial photons is non-elastically scattered. In other words highly sensitive equipment (lasers, detectors, filters), what usually means also quite expensive, is demanded.

One more disability is eventual damage or laser-induced degradation of a sensitive or light absorbing sample (especially when examining unknown matter) through intensive laser radiation however experienced analysts can anticipate this complication in the right preference of measurement procedure.

V. APPLICATIONS

Raman spectroscopy has been reborn in recent years. As the more sophisticated spectroscopic and computer technology access increased, Raman spectroscopy has become a tool for not only purely research, but also for contrivable routine industrial analyses. These days, Raman spectroscopy finds applications, which number is still rising, in variety scientific and industrial disciplines and branches such as:

- **Material sciences** including semiconductor industry, nanotechnology, solid state physics, synthetic polymer materials and others. 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 crystalline, transparent, non-transparent samples, samples with different surface textures).
- **Nanotechnology.** Raman spectroscopy is suitable technique for characterization of nanomaterials as nano-composites, nano-sized crystals, polymers and semiconductors developed in a form of films, wires or dots or modern and ancient ceramics. The method provides determination of nanocrystals, chirality, semidiameters in nanomaterials, also characterizing micromechanical behavior or synthesis processes control (polymer curing, laser ablation, electrochemical deposition). It is a good tool for mapping and probing nanophases dispersed in matrix.
- **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.** Raman spectroscopy systems find application in material characterization, finding the crystallographic orientation, etc.
- **Synthetic polymer materials.** Raman spectroscopy serves for real-time monitoring of polymerization reactions for the purpose of controlling the processing time, for plastic identification for recycling purposes, measuring the thickness of polymers such as protective and coating films, evaluation of polymer material under applied strain or quality control of incoming/outgoing products.
- **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. Except for identification the method is used for characterization and analyses of organic and inorganic substances, including carbon materials, solvents, films and for chemical processes monitoring.
- **Forensic sciences.** Forensic scientists often deals with really unknown samples that cannot be reproduced, require multiple analyses, but their amount is limited. Raman spectroscopy/microscopy is becoming a tool of major importance in forensic science since it satisfies

most of forensic examination criteria, as are mentioned above in advantages: it is a non-destructive, non-contact method without the necessity of sample preparation and possibility of application on a wide range of materials. In-situ measurements can be realized, meaning no contamination of evidences during taking samples [4]. Raman microscopy brings benefits of optical microscopy, what means that the sample can be surveyed under microscope, particles or locations isolated and consequently their Raman spectra acquired. Method is used for forensic analyses and rapid identification of trace amounts of substances in evidential materials as are paints, inks from documents, pigments, explosive particles, inflammables, drugs, illegal active ingredients, fibers, gunpowder residues, chemical and biological agents, plastics and other various forensic evidences. An example of Raman spectra of cocaine is shown in Fig. 6. In most cases forensic examination comprise comparative analyses, hence the spectra libraries and databases are required. In case of having comparable samples it is easy to demonstrate the match or identify counterfeit for instance of documents or historical artworks.

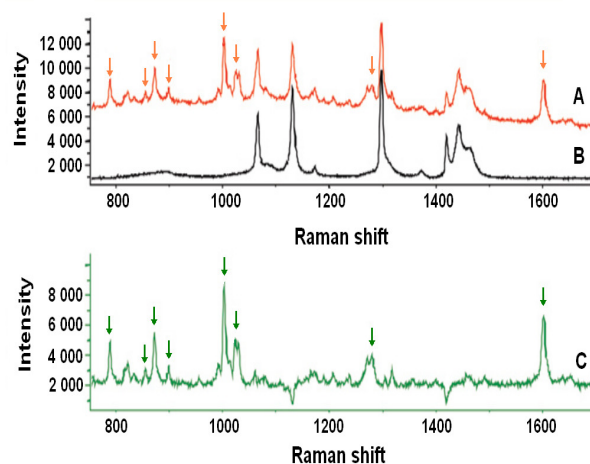


Fig.6 A – Raman spectrum of cocaine in plastic container, B – Raman spectrum of plastic bag, C – the difference spectrum of cocaine obtained by subtraction of spectra A-B.

- **Security forces, fire brigades.** Identification of unknown or hazardous substances, by instance detection of explosives or drugs. These units often work with portable spectrometers enabling identification right in action. Appreciable benefit of method is potentiality of measuring samples through containers.
- **Pharmaceutical industry.** The role that Raman spectroscopy plays in pharmaceutical research, development and manufacturing is still rising. Raman analysis is an efficient tool for control of quality and purity of pharmaceuticals, active substances and excipients (even through packing). Counterfeits pharmaceutical signify a health risk since they may contain harmful impurities, wrong ingredients or incorrect amounts of active pharmaceuticals. Raman

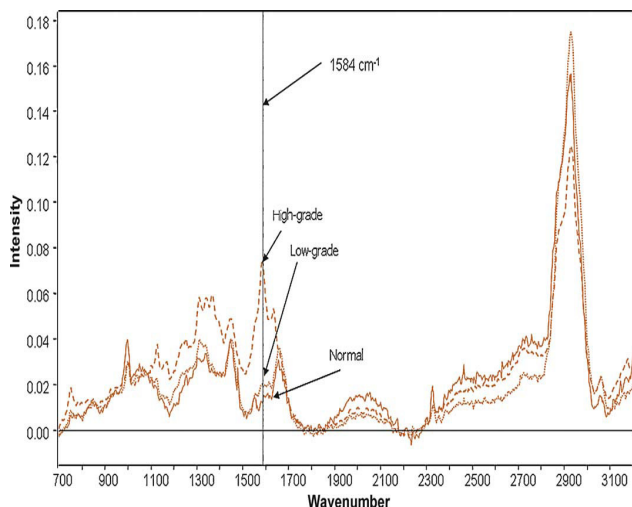


Fig. 7 Raman spectrum of high-grade urothelial carcinoma (UC; dashed) tissue, low-grade UC tissue (dotted), and normal tissue (solid) – the notable peak at 1584 cm^{-1} . [8]

spectroscopy has been also successfully used for adulterated pharmaceuticals revealing.

- **Medicine and biology.** Applications benefiting Raman spectroscopy involve e. g. DNA analyses, prognoses and diagnoses of carcinomas (example displayed in Fig. 7), measuring blood and tissue oxygenation, study of biological systems. With regard to non-destructiveness and contactless the great potential of the method for *in-vivo* medical examination is studied.
- **Food Product.** Raman spectroscopy serves for detecting bacteria and contaminants in food product or measurements of fatty acid unsaturation in food oils and other ingredients.
- **Geology and mineralogy** – Raman spectroscopy serves for identification of the principal mineral phases or classification of rocks, etc.
- **Art.** The main intention of any analytical studies of any ancient artwork should be to get as much information as possible by non-destructive methods. Raman/Micro-Raman spectroscopy is suitable and effective for this purpose. Raman examination of artworks and artefacts (the most often are paintings and pottery) reveals worthy information for conservators or those of general historical interest. Knowledge of artistic materials in connection with the time period or the location in particular region and also about the artists' modus operandi can be gained.

Followed issues are solved at the present time using Renishaw inVia Basis Raman microscope (schema in Fig. 8) with the 514 nm excitation Argon ion laser at Faculty of Applied Informatics, Tomas Bata University in Zlin, Czech Republic.

- The methodology for the detection of small hexavalent chromium concentrations with the use of Raman spectroscopy is developed. Chromium is an element of a common

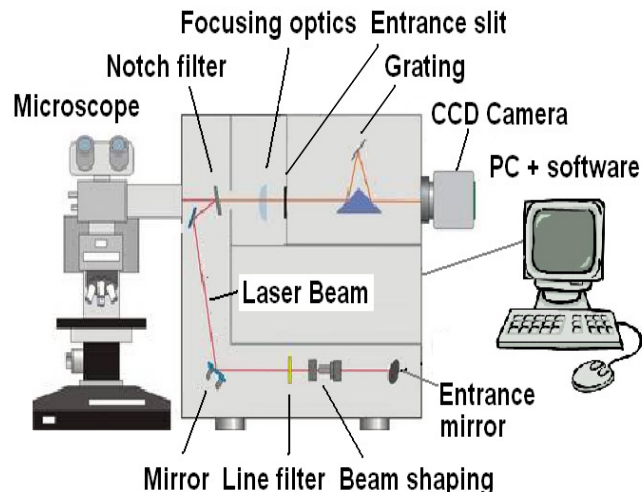


Fig. 8 Schema of Raman spectrometer

occurrence in nature. In living environment can be found in several modifications. The most frequent form is metallic chromium Cr(0), trivalent chromium Cr(III) and hexavalent chromium Cr(VI). 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.[9] 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) [10] (Fig. 9, Fig. 10). Obtained results showed the complication with fluorescence that masks the Raman spectra of chromium compounds contained in natural

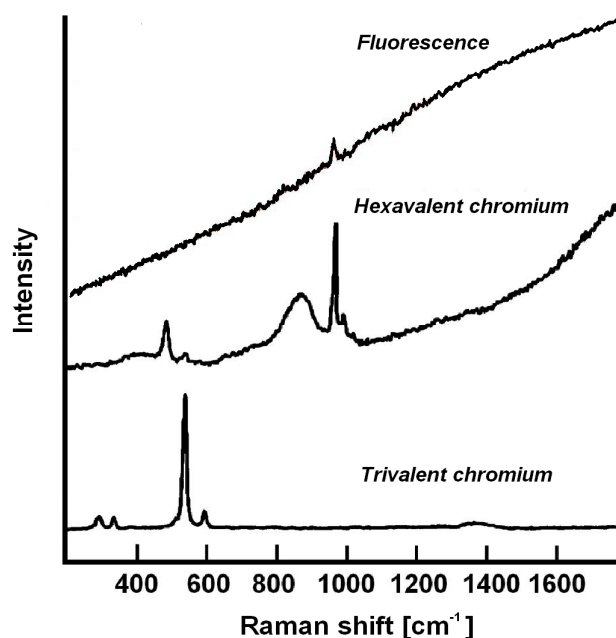


Fig. 9 From above: Raman spectrum masked by fluorescence, Raman spectrum of Cr(VI) and Cr(III)



Fig. 10 Fibers of leather with linked hexavalent chromium

polymers. This situation has been so far solved by bleaching – prolonged illumination of the sample before own measurement, but without success. On the other hand, shortening the exposure time to tenths of seconds allowed recording of the Raman spectra.

- Raman spectroscopy has been applied on monitoring of the curing process of epoxy resins. Epoxy resins are one of the most versatile polymers with a number of good to excellent properties and owing to them are epoxy based materials intensively applied in many technical areas and industries. Due to a time series measurement can the kinetics of crosslinking be controlled and the changes in active chemical groups and bonds recorded and analyzed. The progression of crosslinking process dependence on temperature has been also studied. In Fig.11 is displayed 3D map of crosslinking reaction at the temperature 25°C recorded over 30 minutes with evident peak corresponding to gelation time.
- 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 affect properties of electric conductivity of different forms of carbon (Fig.12.), 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 are used for shielding electromagnetic fields or elimination of static charge and others.
- Determination of inks within the scope of security usage is an upcoming problematic at present time dealing with the possibility of revealing ink document falsifications. Ten different blue ball-pen inks with the known producer were examined for the purpose of ink identification and aging and eventual document dating. Actual results show

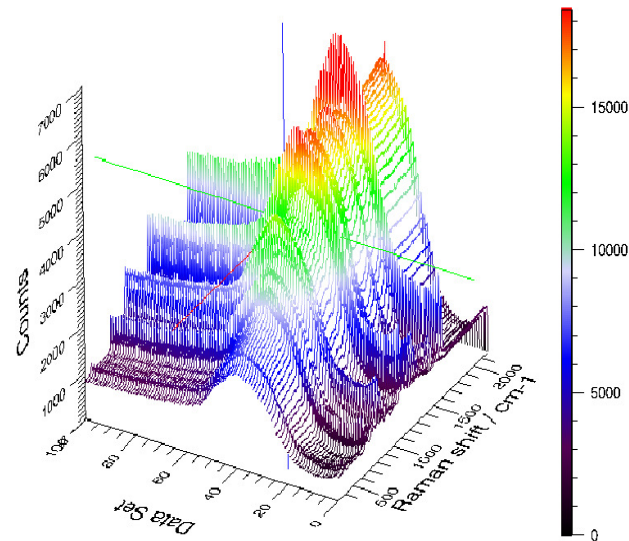


Fig. 11 3D map of epoxy resin crosslinking process

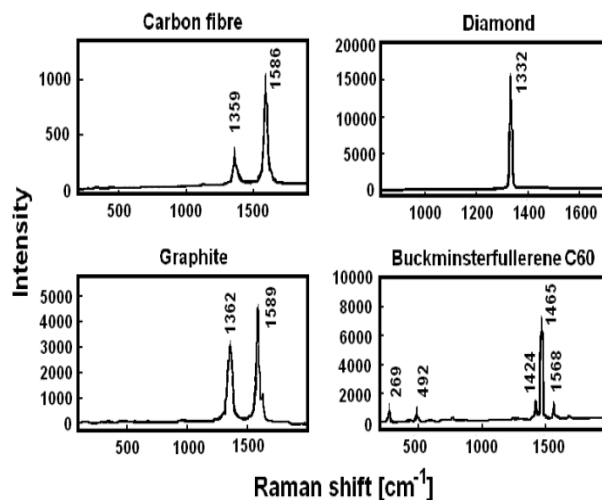


Fig. 12 Raman spectra of different modifications of carbon

very similar Raman spectra at the inks from the same producer e.g. KOH-I-NOOR, other are comparable with a few differences, which, however, should be sufficient for the identification. Two samples were sheltered by strong fluorescence and despite different setting of measuring parameters, Raman spectra was impossible to obtain. This can be after all also a sort of hint for identification following by other methods.

- Another application deals with the mapping of the distribution of active substances in pharmaceuticals. In Fig. 13 and Fig. 14 are for illustration shown 3D maps of distribution of acetylsalicylic acid and ascorbic acid in a Aspirin.

Other applications are prepared in present time.

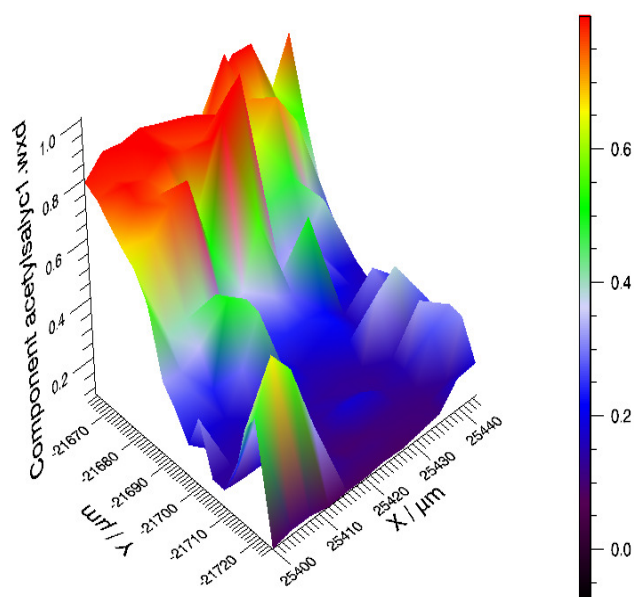


Fig. 13 3D map of acetylsalicylic acid in Aspirin.

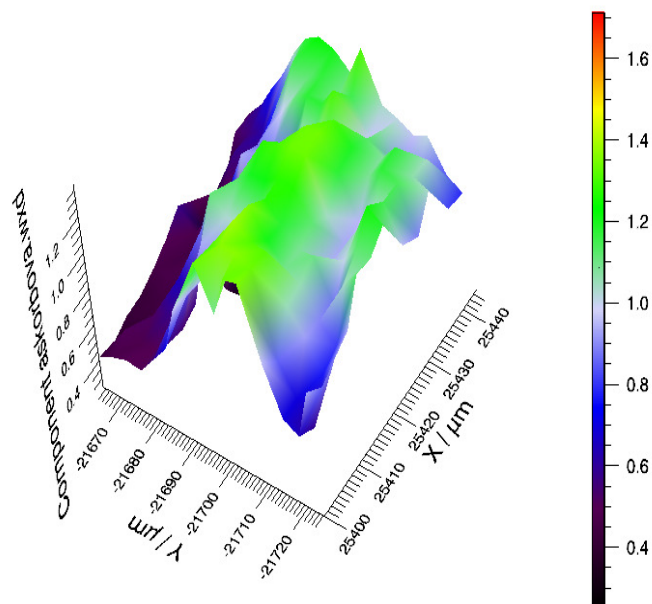


Fig. 14 3D map of ascorbic acid in a Aspirin.

VI. CONCLUSION

Raman spectroscopy is rapidly progressing method. Raman/ Micro-Raman spectrometers are becoming essential and unnecessary equipments for researchers in variously specialized laboratory such as forensic, pharmaceutical, laboratories, for development of nanomaterials, laboratories focused on examination of artworks or for controlling products.

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. Actual applications were highlighted to demonstrate great potential of the method. Laboratory program for forensic applications, mechanical properties and aging of solids is preparing at the present time.

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