

Non-destructive spectroscopic methods for gem analysis: a short review

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Abstract – Since antiquity, gems fascinated worldwide cultures, being used for adorning jewels or precious objects. Gems analysis primarily aims to determine identity, origin (natural or synthetic) and geographic or geological source of a gem, which in turn define its value. In view of preciousness and rarity of gems, their analysis requires the use of non-destructive or micro-destructive methods, some of which might be limited when gems are mounted in jewels. Beside traditional gemological tools and laboratory instruments, portable/mobile analytical methods are especially useful to study gems in jewelry collections or to characterize gems in field. Portable Raman spectroscopy emerged as a powerful technique in gems analysis; it allows a rapid identification of a gem, providing also insights on other relevant aspects for its classification; however, origin and provenance can be only hypothesized through the analysis of solid and fluid inclusions by laboratory apparatus. The determination of trace-element chemistry by using portable X-ray fluorescence might overpass this limit, providing the chemical fingerprint of the geological and geographical origin of a gem. In some cases, advanced and micro-destructive analytical techniques enable more precise and certain gem classification. This short review intends to provide an overview on the potential of non-invasive and non-destructive complementary spectroscopic methods useful for studying inorganic and organic gemological materials.

I. INTRODUCTION

The incorporation of advanced methods into the gem analysis routine requires the exploration of instrument's efficiency and performance, the development of databases and the establishment of analytical protocols. Several researches demonstrated the potential of portable Raman spectroscopy in gem analysis [1-11]. These studies proved the ability of the method in rapid and non-destructive gem identification, providing also information on enhancement treatments and clues on gems origin. Nevertheless, origin and provenance characterization

require the use of laboratory micro-Raman equipment for the identification of solid or fluid inclusions and/or the analysis of peculiar spectroscopic regions (e.g.: OH region in emeralds for the estimation of alkali ions amount [2] or CH₂ and CH₃ groups in fossil resins [3]). Researches on several precious organic and inorganic gems evidenced the complementarity of Raman spectroscopy and other spectroscopic techniques, such as portable X-ray fluorescence (e.g.: for the chromophores identification in colored inorganic gems or the origin and provenance determination through trace-element chemistry [4]) or ¹³C solid state nuclear magnetic resonance (e.g.: chemical fingerprint and maturation degree in fossil resins [3]). Portable spectroscopic methods coupled with laboratory equipment and - in some cases - with micro-destructive analytics can be thus routinely used in the analysis of gems in their rough or polished/cut state; otherwise, the characterization of mounted gems on precious objects or unmovable artworks preserved in Museums requires the application of mobile equipment. Measurement campaigns carried out on jewel collections in Sicilian Regional Museum (e.g.: *M. Accascina* and *P. Orsi* Museums in Messina and Siracusa, respectively) emphasized the potential of portable Raman instruments for the identification of gems [5-6]. Numerous analyses carried out in a really short time and with different excitation wavelengths on a large number of artifacts (necklaces, earrings, rings, brooches, hair clips, precious belts and loose engraved gems) enabled the fast classification of precious and semi-precious gemological materials, enabling the identification of interesting gems and revealing misclassifications.

II. COLORED INORGANIC GEMS

A. Gem identification

Rubies, sapphires and emeralds are among the most fashionable colored gems. Rubies and sapphires are the red and the blue corundum (Al₂O₃) varieties. In rubies the color is due to Cr³⁺ ions which produces pale pink

through deep red hues; in sapphires the Fe^{2+} - Ti^{4+} pairs and Fe^{2+} - Fe^{3+} give the blue hue. A wider range of colors (green, orange or purple) is produced by the combination of these primary chromophores. Emerald is a green beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) which color is due to chromium and vanadium traces replacing aluminum. The imitation of valuable and rare gems by other natural mineral species or composite gems is very common; synthetic gems having identical appearance, atomic structure and very similar chemical composition with respect to natural counterpart can be also created in laboratory. In addition, gem color, luster, transparency and clarity are often modified by enhancement treatments, some of which altering the nature of the gem and, in turn, its value.

In studying colored inorganic gems, the first question to answer is its mineralogical identity. Rubies, sapphires, emeralds and their common simulant are well-defined mineral species, so that Raman spectroscopy can easily and rapidly answer to this question (Fig.1) [2,7-8].

Laboratory and portable equipment can be both used for this scope. Otherwise, micro-Raman laboratory instrument are required for origin and genesis determination or specific enhancement treatments identification.

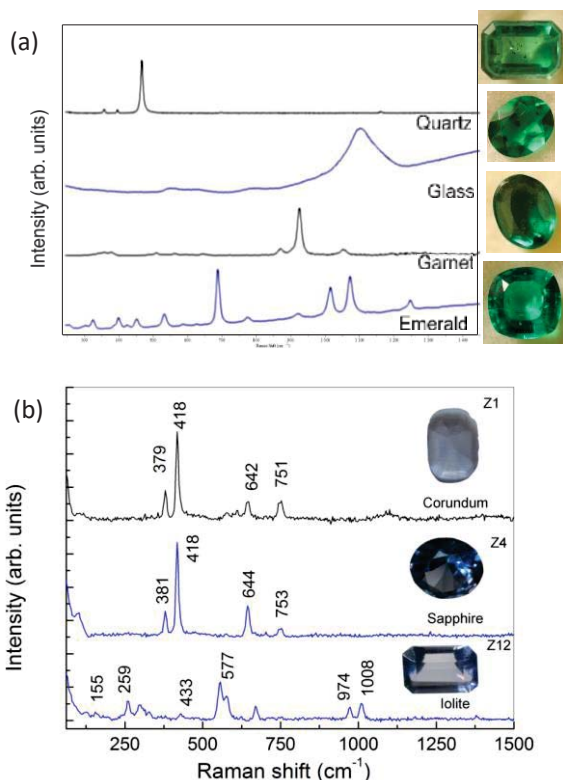


Fig. 1. Raman spectra collected on different (a) green and (b) blue gems enabling the identification of their mineralogical identity [2,7].

B. Origin and genesis

In emeralds, genesis (natural vs synthetic) and origin (geological environment) can be studied by investigating OH stretching modes spectral regions, which reveals the presence of alkali ions in the beryl channels (Fig.2) [2]. Bands centered at about 3608 and 3598 cm^{-1} belong to water type I (without alkali nearby) and water type II (with alkali nearby), respectively. The presence and the intensity of the band at 3598 cm^{-1} , as well as the I_{3598}/I_{3608} ratio, depend on the amount of alkali ions. Schist type emeralds – which originate from metamorphic rocks or pegmatites close to mica schists and gneiss - are high-alkali; otherwise non-schist type occurring in pegmatites related to granitic formations are low-alkali [2]. No Raman bands are expected in this spectral region for the flux grown synthetic crystals, being formed in the absence of water. Hydrothermally grown synthetic crystal should display only alkali-free water (type I).

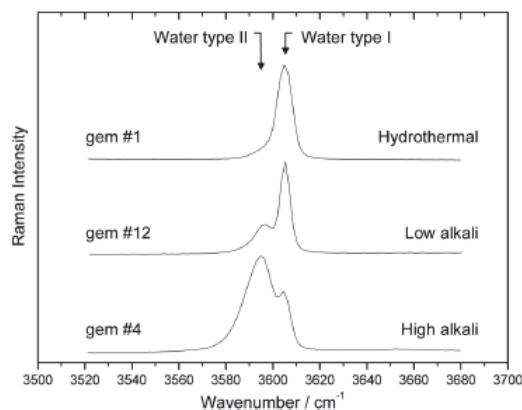


Fig. 2. Raman spectra of three green gems with different origin in the OH stretching region. From [2].

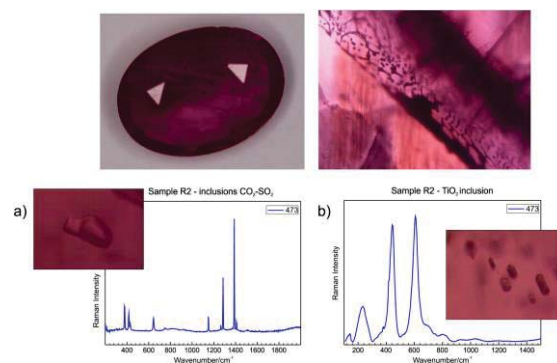


Fig. 3. (a) Fluid and (b) mineral inclusions in a natural ruby. Pictures and Raman spectra are shown. From [8].

In red and blue corundum gems, clues on origin and provenance can be provided by the analysis of solid and fluid inclusions through laboratory equipment (Fig.3) [7-

8]; for example, Burmese and Afghan marble-hosted rubies are characterized by calcite inclusions; otherwise, the typical mineral inclusions in rubies from Vietnam are calcite, dolomite, rutile, diaspore, phlogopite and zircon. Very specific inclusions allow to identify rubies from Sri Lanka; in fact, they are characterized by very characteristic flakes of biotite and rutile needles [7-8].

Moreover, the inclusion analysis might reveal invasive enhancement treatments in natural gems (Fig.4).

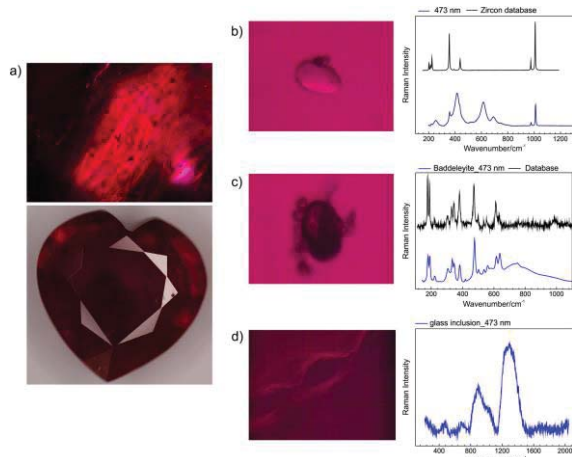


Fig. 4. Inclusions in a natural glass filled ruby. mineral inclusions of suggest subsolidus reactions of zircon with the subsequent formation of baddeleyite. From [8].

However, the solely Raman spectroscopy analysis prevents a certain origin classification of corundum gems; otherwise, trace-element chemistry has been proven to be to be useful in determining provenance and origin of rubies and sapphires (Fig.5) [4]. In rubies, Cr is expected to be the most abundant element, being responsible for the color; Cu is usually considered a proof of synthetic origin even if can be found also in natural rubies within sulfide inclusions; Ga is usually absent in synthetic corundum; higher content of Ti, V and Fe characterize natural corundum compared to synthetic ones.

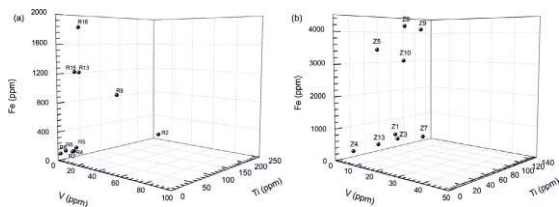


Fig. 5. Example of origin discrimination of natural and synthetic (a) rubies and (b) sapphires based on Ti-V-Fe trace-element chemistry obtained through p-XRF. From [4].

III. ORGANIC GEMMOLOGICAL MATERIALS

A. Pearls

Pearls are particularly fascinating organic gems, formed by mollusks secreting carbonates. They are complex objects, being constituted by both inorganic (carbonate polymorphs) and organic (conchiolin fibers and pigments) materials. Several researches attempted to use non-destructive methods for understanding the pearl growth process and providing pearls classification criteria. According to one accredited model, calcite (mainly in saltwater pearls) and vaterite (especially in freshwater pearls) occur in the few millimeters around nucleus, with a sharp transition to aragonite plates constituting most of the nacre. Pearls may be natural, but most commonly are freshwater or marine cultured. In absence of appropriate certification, the naked-eye observation and the inspection under a microscope can help to detect features for which pearls would differ, namely luster, nacre thickness, shape and dimension. Pearls range in color from neutral white, cream and silver to pronounced tones of pink and yellow or natural black purple (e.g.: in Tahitian pearls); when natural, the pigments are transferred to nacre by mollusks. A recent Raman based study carried out on numerous freshwater, saltwater and natural white and colored pearls (Fig.6) by using three different Raman spectrometers (two micro-Raman and a handheld instrument), with different excitation sources (632.8, 532, 473.1 nm), enabled to review and test and most relevant results reported in literature on the Raman analysis of pearls [9].



Fig. 6. A selection of natural, freshwater and saltwater pearls analyzed by Raman spectroscopy. From [9].

As regard pearls classification, the research suggested that Raman spectroscopy alone is not enough to classify and discriminate freshwater and saltwater pearls. Otherwise, the potential of Raman spectroscopy is fully exploited in the study of colored pearls; in fact, the natural pigments in yellowish and pinkish cultured pearls consisting of a mixture of polyene molecules can be easily characterized and discriminated from artificial dyeing agents and/or enhancement treatments.

In respect to the use of different excitation lines, by exciting with different wavelengths, Raman spectra return slightly different information. By using 632.8, 532, 473.1 nm excitation sources, the main features of aragonite in

pearls can be always detected (Fig.7.a); the relative intensity of peaks may change: in general, in the high wavenumber region the signal becomes more intense using shorter excitation wavelengths. Overall, increasing excitation wavelength allowed to getting better spectra. For example, the doublet of aragonite at $702\text{-}706\text{ cm}^{-1}$ can be well resolved only by using the 632.8 nm source (inset of Fig.7a). Resonance effects are very important in the analysis of the natural pigments of pearls; by using 473.1 and 532 nm lines, an increase in the Raman intensity for the main stretching modes of polyene molecules together with their combination and overtone modes can be observed (Fig.7b).

Finally, by comparing laboratory and portable equipment, even if the spectral resolution of a portable spectrometer is worse (e.g.: wider Raman peaks) it is possible to obtain surprisingly good results, enabling the detection of all the aragonite peaks, along with Raman features due to the presence of natural pigments (Fig.8). It can be suggested that the use of laboratory set-up is therefore mandatory only in studies of micrometric details, as well as in the determination of very small band shifts.

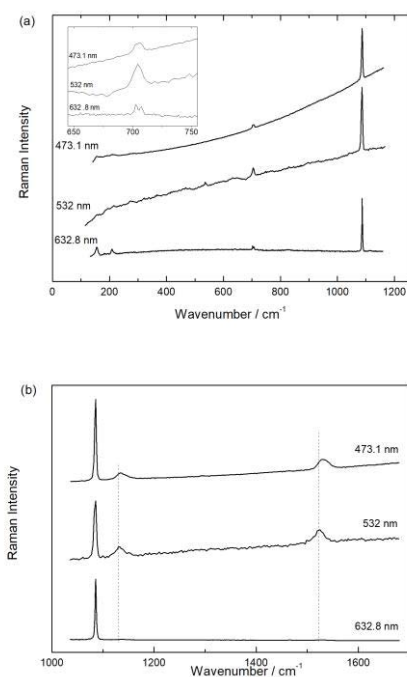


Fig. 7. Examples of Raman spectra collected by using different excitation sources on (a) white Japanese cultured saltwater pearl and (b) Chinese cultured freshwater pink pearl.

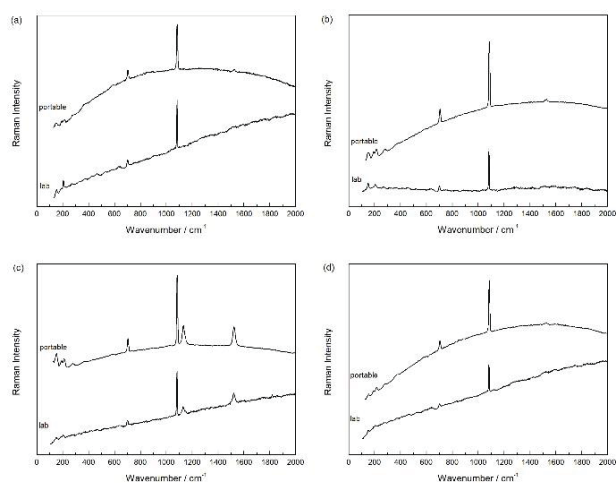


Fig. 8. Comparison between Raman spectra collected by laboratory and portable spectrometers working at 532 nm on different pearls. (a) Japanese cultured saltwater white pearl, (b) Australian cultured saltwater silver pearl, (c) Chinese cultured freshwater pink pearl, and (d) Chinese Mabee cultured freshwater white pearl.

B. Amber

Amber is a fossil resin used since antiquity as gemological material. Fossil resins are plant exudates transformed due to a process known as fossilization. Amber is translucent, from yellow-green to brown-red in color; usually, it contains interesting inclusions such as seeds, leaves, insects, animal remains, mineral crystals and bubbles of air and water. The best known worldwide amber deposits are in the Baltic region of Northern Europe and in the Dominican Republic. Sicily is also a source of a rare and fashionable amber, mainly founded along the hydrographic basin of Simeto River, from which it takes its name *simetite*. The chemical fingerprint of ambers depends on both the biological origin and the geological environment in which the fossilization processes took place.

The characterization of fossil resins' chemical fingerprint and the determination of their maturation degree – which in turn enabled a provenance determination – can be achieved by Raman spectroscopy [3]. In fact, maturation, aging, and oxidation degree of resins imprint specific spectroscopic regions which analysis enables the discrimination of different ambers (Fig.9). The intensity ratio $I_{1650}/I_{1450} > 1$ characterizes immature resins, while a ratio < 1 indicates mature fossil resins; this happens because the 1650 cm^{-1} band is attributed to C=C stretching, and its decreasing is due to the unsaturation of resin as the fossilization process proceeds. Bands at about 710 and 740 cm^{-1} are typical of immature resins and tend to disappear with the maturation process. In recent studies, the comparison

among Dominican, Baltic and Sicilian ambers evidenced that the solely Raman intensity ratio cannot be used as discrimination criteria; in fact, the I_{1650}/I_{1450} value and the rate of maturation is not just a function of time but is also related to the burial environment. Otherwise, the contribute of the overall spectroscopic fingerprint has to be taken in account; statistical analysis provides, in this sense, interesting results [3].

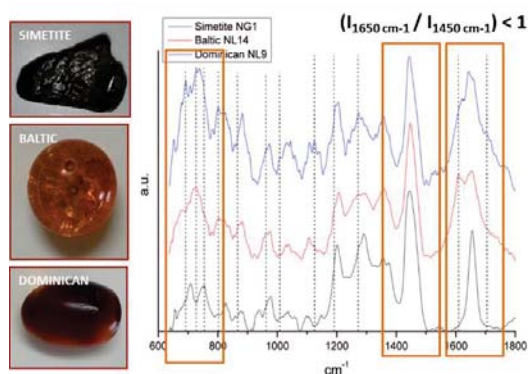


Fig. 9. Examples of Raman spectra collected on Sicilian, Baltic and Dominican ambers. The main relevant differences are due to: well-structured band at 1645 cm^{-1} in simetite, doublet ($1655, 1609\text{ cm}^{-1}$) in the Baltic amber; band at 1644 cm^{-1} with a shoulder in the Dominican one; doublet in simetite at $\sim 710\text{--}750\text{ cm}^{-1}$, only one band in Baltic amber (730 cm^{-1}), triplet in the Dominican amber ($690/720/750\text{ cm}^{-1}$).

When micro-sampling is allowed, a detailed chemical characterization of amber can be achieved by the application of ^{13}C Solid state NMR spectroscopy. In general, the NMR spectra of ambers can be divided into three regions: single-bonded carbon ($-\text{C}-$) in the region $90\text{--}10$ ppm, double-bonded carbon ($>\text{C}=\text{C}<$) in the region $155\text{--}105$ ppm, carbonyl and carboxyl groups in the region $200\text{--}170$ ppm. In the double-bonded carbon regions, the relative intensity of resonances peaks related to di- and tri-substituted alkene resonances (at 128 and 140 ppm) and exomethylene (at 110 and 150 ppm) can be used for esteem maturity of fossil resins; in detail, the relative intensity of these two signals decreases with increasing sample maturation. Studies on Baltic, Dominican and Sicilian ambers evidenced the potential of ^{13}C Solid state NMR spectroscopy in discriminating different fossil resins, especially when the method is coupled with Raman spectroscopy and data are treated with statistical methods [3].

IV. GEMS IN JEWELS AND JEWELLERY MUSEUM COLLECTIONS

The analysis of rare minerals preserved in

mineralogical collection or gems mounted in jewels and preserved in Museums usually aims to define their identity, discriminate genuine gems from imitations and identify possible fakes or forgeries in ancient jewels or art objects [5-6, 9-11]. In all these cases, gems cannot be removed from the objects or damaged, so that restricted methods can be used.

At the Paolo Orsi Regional Museum (Siracusa, Sicily) the well-known *Medagliere* section preserves a noteworthy and valuable quantity of gems and jewels, mainly dated to Hellenistic and Roman Age. More than 700 engraved gems and numerous jewels come from both private collections and archaeological excavations. Uncertainties in attribution, authenticity and dating of some of these objects required a diagnostic in situ campaign [5]. Portable Raman spectroscopic analysis by using different excitation wavelength enabled the identification of a large variety of precious and non-precious materials, including important gems as diamonds, rubies, garnets and emeralds (Fig.10); in some cases, gems of great archaeological relevance were re-attributed. Among engraved gems, silica varieties were predominant (Fig.11); in mounted gems, numerous garnet-almandine were identified based on their Raman fingerprint [5].

The M. Accascina Regional Museum (Messina, Sicily) preserves jewels consisting in precious and unique ex-voto jewels made by Messinian goldsmiths during the 17-18th centuries, which resembled the more famous Trapani and Palermo jewelry production. During the centuries, they suffer forgeries, attested since 1950s, so that gem analysis was required for their classification. Portable Raman analysis enabled the identity identification of numerous gems classified as topaz, agate, diamond, ruby, emerald, pearl, and glass [6]. Raman analysis also revealed misclassification (especially for the most valuable gems such as topaz, diamonds and rubies) and detected different simulants (quartz, colorless or red glass, doublets, spinels, and almandine garnets) (Fig. 12). It is appropriate to note that the characterization of metals in jewels and jewelry collections requires the use of portable XRF method.

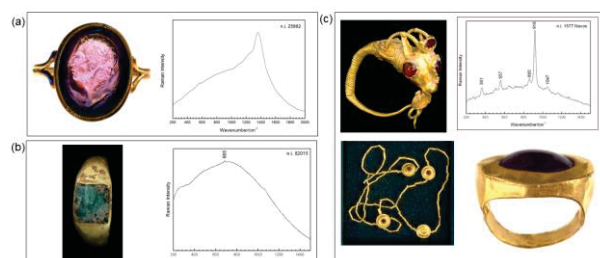


Fig. 10. Pictures and Raman spectra of some jewels from the Medagliere at Paolo Orsi Museum [5].



Fig. 11. Some of the numerous engraved gems which characterization enabled the identification of different quartz varieties.

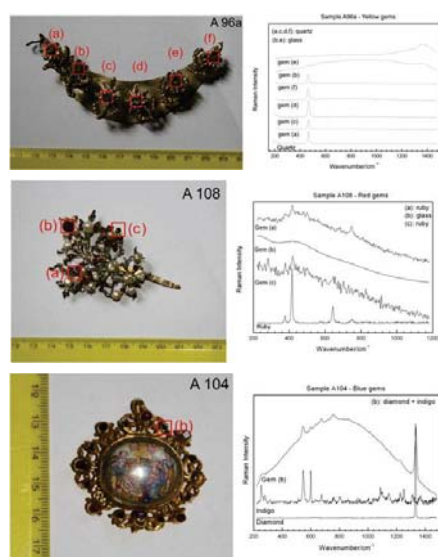


Fig. 12. Pictures and Raman spectra of some of the jewels analyzed at Museo Accascina. From [6].

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