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Raman Spectroscopic Applications to Gemmology

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I. INTRODUCTION

Gemmology is a science which is in special demand for destruction-free methods. Classical gemmology consisted of mainly taking the specific gravity of a stone, analyzing it in the microscope, and taking refractive indices and absorption spectra of the stones. Tests which are common in mineralogy, such as hardness tests, etching the stones with acids, taking thin sections for the microscope, and so forth, are not applicable for gemstones.

When analytical methods became more available, it was mostly spectroscopic methods in different areas of the electromagnetic spectrum which enabled the gemmologist to study the stones in more detail. Good gemmological laboratories nowadays are equipped with ultraviolet-visible (UV-vis) spectrometers, Fourier transform infrared (FTIR) spectrometers (without microscope attachment) and, less frequently, energy-dispersive x-ray fluorescence (ED-XRF) spectrometers. All of these methods can be applied to identify the nature of single crystals, but they are macro methods which give information about the whole stone or the surface of the stone. Generally, they cannot be directed onto a small area of the stone.

Another quick and destruction-free method for identifying gemstones is the use of Raman spectroscopy. Most Raman spectrometers are equipped with a microscope which enables the gemmologist to focus on the spot to be analyzed. The confocal system of the Raman spectrometer then allows an analysis of the chosen spot, which can be as small as $2\mu\text{m}$. This combination between microscopic observation and Raman analysis makes it a micro method especially useful for the gemmologist, because inclusions often help to determine the authenticity or even the origin of a gemstone. Also, gemstone treatments like the filling of fissures in emeralds, can be identified using micro-Raman analysis.

Most materials that the gemmologist or mineralogist will encounter have a typical Raman spectrum, serving as a "fingerprint" for that type of material. One major subset of materials that rarely give characteristic spectra due to their bonding characteristics are certain metals and alloys. In addition, subtle changes within one material such as alterations in crystallinity and composition can often be detected.

In gemmology, Raman spectroscopy has been used by French scientists for more than 20 years [1], but for gemmological laboratories, the instruments on the market were too large and too costly. For several years now, smaller Raman spectrometers are available, which can be placed on a workbench and, thus, are more user friendly. Since then, more and more gemmological laboratories are using this technique in addition to their traditional methods, and the number of publications in this field is growing [2–13]. The following sections demonstrate the applications of Raman spectroscopy in gemmology.

II. METHODS OF ANALYSIS

For the analysis of gemstones with Raman spectroscopy, certain requirements are necessary: it is important that only little sample preparation is required. The samples are placed on a microscope stage after they have been mounted on a glass slide. Using the optical microscope together with an external light source, the area to be analyzed is brought into focus before switching to laser light.

The Raman studies presented here were performed using a Renishaw Raman System 1000. This instrument, among others, possesses important properties that makes it useful in a gemmological laboratory:

1. The modern Raman spectrometer does not take up as much room as previous models; that is, it fits on a workbench.
2. The Raman spectrometer is equipped with a Peltier-cooled charge-coupled device (CCD) detector, together with a laser which can be selected depending on the application. The 25-mW air-cooled argon ion laser (Spectra Physics) lasing at 514 nm is the most versatile for gemstone work.
3. A good quality optical microscope equipped with a selection of objectives objectives (see also Ref. 10) and various light sources (transmission, reflection, external light source such as fiber light) allows the exact positioning of the area to be analyzed.
4. Raman spectroscopy can be used as a confocal method together with a microscope. The area to be analyzed may be on the surface of an object or inside a transparent object. Once it is in focus of the light microscope, the exciting laser source is also focused on this spot so that the analysis can be performed. Figures 1a–1c illustrate the pathway of the laser beam through a hiddenite crystal, which produces a sharp fluorescence trace of the incident laser light. First, the laser beam is focused on the surface of the sample, then in the middle of the sample, then on the bottom of the sample.
5. Using a static mode or the "extended scanning" facility, a whole spectral range, depending on the target, can be recorded at a specific resolution.
6. A modern software package allows one to collect and store the Raman spectra, as well as data analysis, presentation, and the ability to compare the collected data with reference spectra stored in a database.

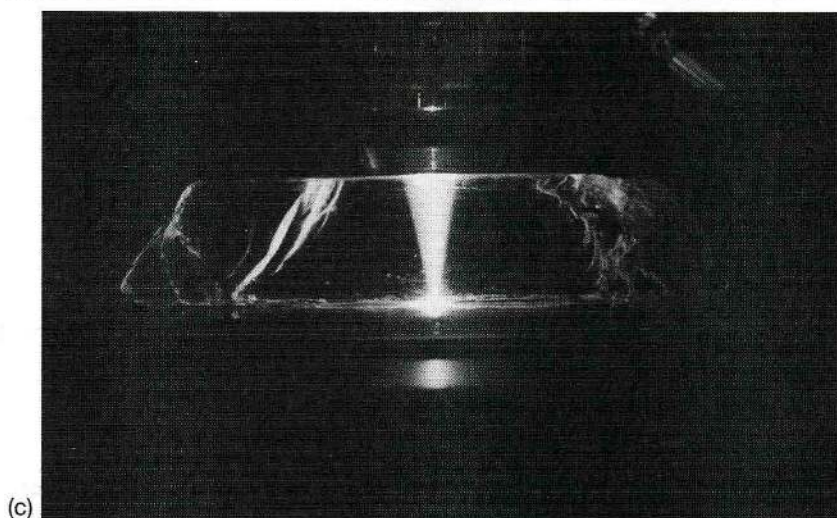
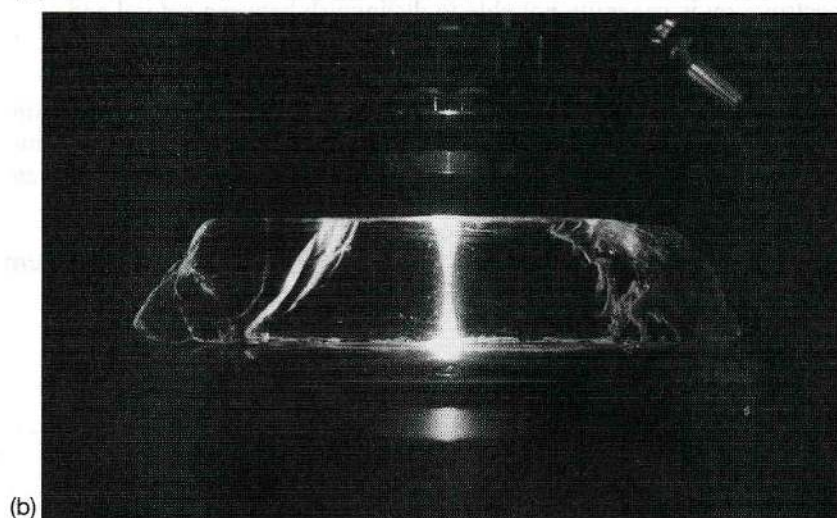
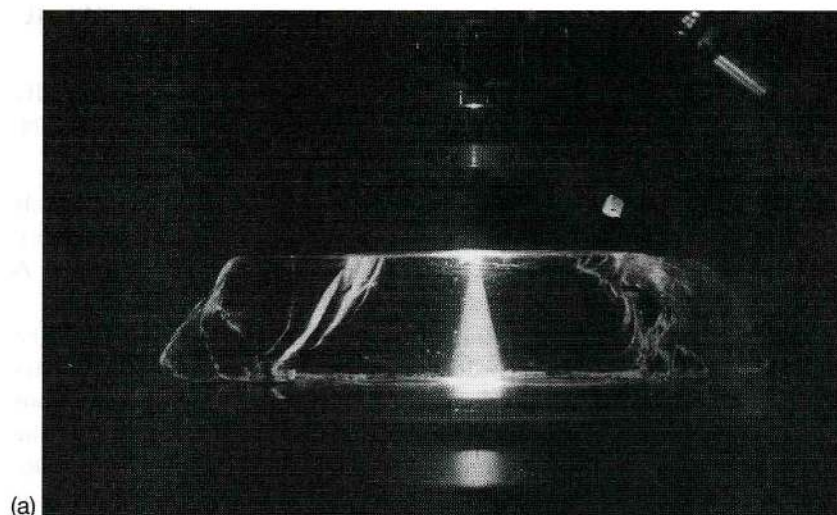


Figure 1 A hiddenite crystal showing the focusing point of a laser beam during Raman analysis: (a) the focus is on the top of the sample; (b) the focus is in the center of the sample; (c) the focus is on the bottom of the sample.

Because gemstones are mostly single crystals of silicate minerals, there is generally no need for a long exposure time. This makes gemstone analysis quick and efficient. Difficulties may, however, arise under certain circumstances:

1. Microcrystalline substances such as turquoise or opal and other certain minerals may have a high background with the 514-nm laser generally used for gemmological samples. Therefore, characteristic Raman peaks are difficult to obtain. A careful background subtraction should be applied to obtain reasonable results.
2. Some minerals display anisotropy of Raman peak intensities, depending on the optical direction in which they are recorded (see also Chapter 9). Figure 2 shows the Raman spectra of an albite crystal in three different directions. It is obvious that, although the peak positions do not change, the intensities of some of the peaks are different. This may lead to misinterpretation when a stone is not accessible from all sides, so that only one of the directions can be analyzed.
3. Raman spectroscopy is generally not able to distinguish between natural and synthetic gemstones such as natural ruby or synthetic ruby, except where typical inclusions are present, which can then be analyzed (see Sec. III.B).
4. When a sample is mounted on a soft medium such as "Blu Tack," this medium may move during analysis and the focus may shift. Also, larger or roundish samples may move when they are not fixed in one place. For samples with more than

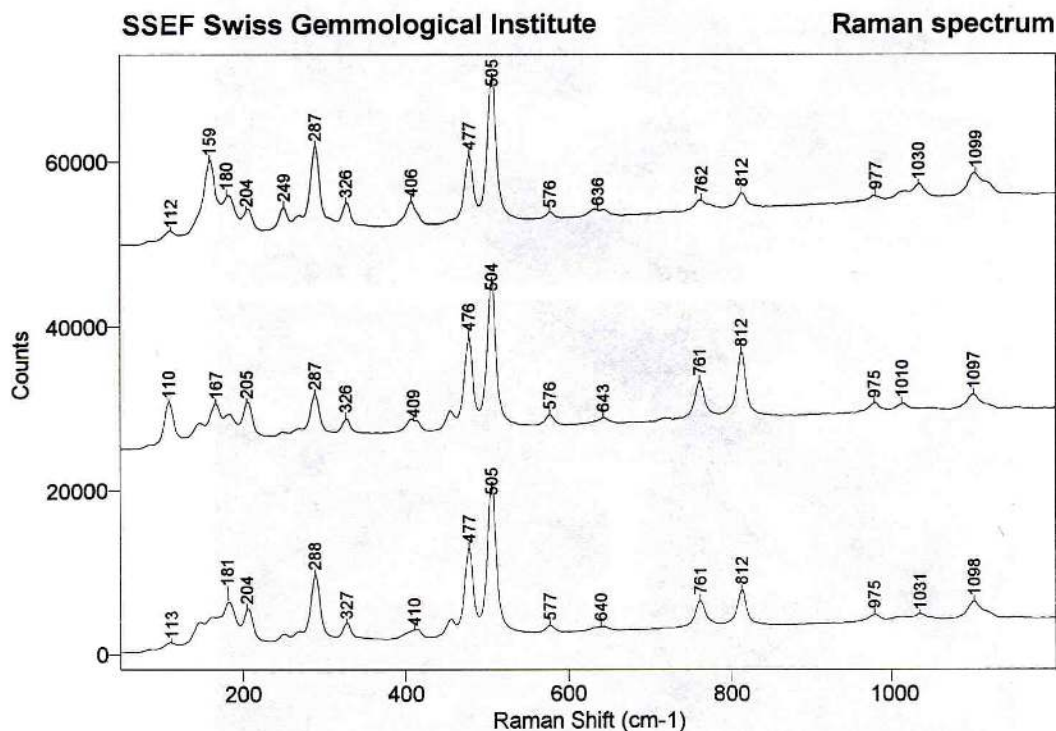


Figure 2 Raman spectrum of an albite crystal recorded in three different crystallographical directions perpendicular to each other (x , y , z). The directional recording of spectra shows anisotropy with respect to the peak heights, but not the peak positions.

one mineral phase, this may give wrong results, whereas monomineralic samples will show higher background signals and lower peak intensities.

5. The mounting medium may display its own characteristic spectrum, which may interfere with the spectrum of the stone to be analyzed, especially if the stone is very small. "Blu-Tack," for example, exhibits a high Raman fluorescence, which may subdue the Raman spectrum of the gemstone under analysis.
6. When analyzing inclusions in gemstones, not only is the Raman spectrum of the inclusion recorded but also a spectrum of the host. The intensity of the overlying spectra depends on several factors such as depth of inclusion in the host (the closer the inclusion is to the surface of the sample, the better its spectrum) and the intensity of the spectrum of the inclusion may be weaker than the intensity of the spectrum of the host. One such example are inclusions in diamonds, which would not give any intensities due to the high intensity of the major diamond peak at 1332 cm^{-1} . Choosing an analysis range which excludes this major peak does, however, produce useful results [13].
7. Gemstones are cut with diamond powder or SiC and polished with Cr_2O_3 , Al_2O_3 , SnO , and so forth. When fissures or cavities are present in a stone, they may be filled with these substances. Peaks from the powders may overlay the Raman spectrum [9] of the host and lead to misinterpretation.

III. APPLICATIONS OF RAMAN SPECTROSCOPY IN GEMMOLOGY

A. Raman Analysis on the Surface of Samples

Many gemstones which are submitted into a gemmological laboratory are loose stones and can generally be identified with classical gemmological means such as refractive index, specific gravity, and diagnostic visible absorption spectra obtained with a hand-held spectroscope. These methods may, however, become time-consuming when a lot of gemstones has to be tested, when they have similar properties, when they consist of several phases, when they belong to a solid-solution series, when they have a rough surface, when they are very large, or when they are set in jewelry.

1. Raman Analysis on a Lot of Gemstones

If a high number of gemstones has to be identified, Raman spectroscopy has proven to be quick and efficient. The stones can be mounted on a glass slide, and a 10-sec or less analysis of the surface of the gemstone is mostly sufficient to obtain an interpretable result. With this method, it is possible to determine if all stones in one lot are of the same gemstone species or if another gemstone or glass is mixed in with the other stones. Raman spectroscopy cannot, however, distinguish between natural and synthetic stones of the same chemical composition, except when flux material is caught and can be analyzed.

Another example is a mixed lot of faceted Burmese gemstones which were given to one of the authors (HH) for analysis. They were mounted on a glass slide and analyzed. In this way, a distinction could be made between seven types of gemstone in the lot. A much larger lot of rough gemstones from Madagascar was also available and was mounted and tested in the same manner. Of 20 stones of different color, 12 different gemstone species were identified (Fig. 3). An important prerequisite to obtain optimal results of these gemstones is that the area where the analysis is performed is perpendicular to the analyzing laser beam; that is, best results are obtained when the focus point is the highest point of

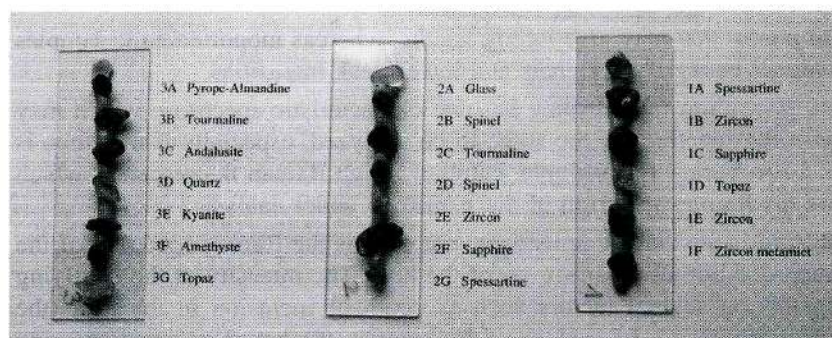


Figure 3 These 20 rough gemstones from Madagascar were analyzed with the Raman spectroscopy. The identification based on Raman spectroscopy is indicated.

the roundish pebble. When this cannot be achieved, not all the light is reflected back into the objective lens and the signal becomes weaker.

When analyzing loose stones, care must be taken that the mounting material does not interfere with the spectrum of the gemstone, because it may possess additional spectroscopic properties such as a high-background signal subduing the signals from the stone or additional peaks leading to misinterpretation of the spectrum. Difficulties with high-background signals are also encountered during the analysis of microcrystalline (e.g., turquoise, magnesite) or amorphous materials (e.g., opal).

2. Raman Analysis on Taaffeite and Musgravite

Due to an overlap of gemmological properties, time-consuming mineralogical research techniques such as quantitative chemical analysis or x-ray diffraction are needed for a determination of the structurally related Be–Mg–Al-oxides taaffeite ($\text{BeMg}_3\text{Al}_8\text{O}_{16}$) and musgravite ($\text{BeMg}_2\text{Al}_6\text{O}_{12}$). To evaluate possible determinations of taaffeite and musgravite by micro-Raman spectroscopy, six taaffeites from Sri Lanka and small musgravite crystals from the Musgrave Ranges, Australia and from Casey Bay, Antarctica were examined. For all samples, quantitative chemical analyses (EMP) were available to identify them as taaffeite or musgravite.

The taaffeite samples were faceted gemstones and were mounted on a glass slide for analysis, as described earlier. Focusing the laser beam onto the sample surface gave satisfactory results, although taaffeite shows similar Raman fluorescence to red spinel with a high background between 150 and 800 cm^{-1} . The small musgravite crystals were stuck on a glass slide with glue, which was then polished down to obtain a smooth surface. This sample preparation was, although not necessary for Raman analysis, helpful because the polishing effect decreased the background to a certain extent. A unique type of Raman spectrum for all taaffeites examined was observed (Fig. 4a), with the six strongest Raman lines at 415, 435, 447, 703, 758, and 809 cm^{-1} . The musgravite samples revealed another typical Raman spectrum with their six major peaks situated at 412, 443, 489, 660, 713, and 803 cm^{-1} (Fig. 4b; see also Ref. 12).

It is notable that although there are small differences in peak intensities related to orientation of the specimen, the overall pattern of the spectrum (in terms of peak positions and peak shapes) of taaffeite is distinctly different from that of musgravite. Consequently,

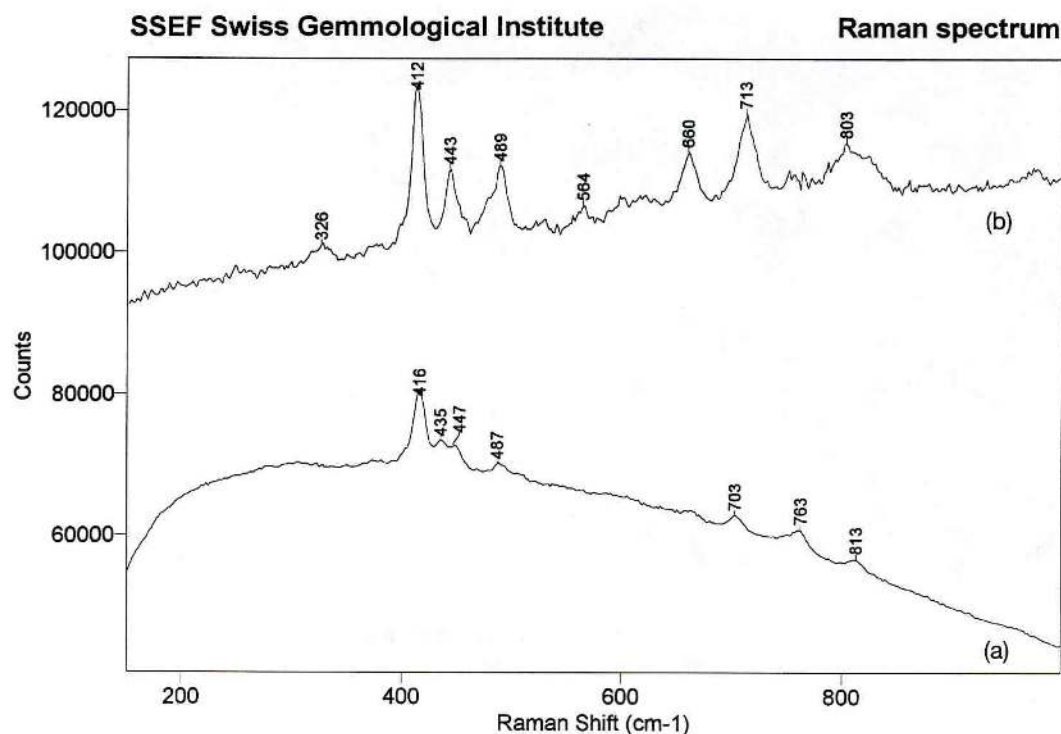


Figure 4 Raman spectra of (a) taafeite, Sri Lanka, and (b) musgravite, Antarctica.

Raman spectroscopy is useful as a nondestructive routine technique for rapid distinction of taafeite and musgravite.

3. Raman Analysis on a Purple Jadeite Consisting of Jadeite and Albite

A violet cabochon-cut gemstone was purchased in Mae Sot (Thailand), a marketplace for Burmese gemstones. The dark violet color and the unusual microscopic structure together with a specific gravity which did not fit with any gemstone made further analysis necessary. A reflected light image indicates two phases in the material (Fig. 5). In a groundmass with a lower luster, needlelike crystals are observed. Micro-Raman spectroscopy on the surface of the sample quickly identified the needlelike crystals with higher reflectance as jadeite and the groundmass with lower luster as plagioclase feldspar. The closest coincidence of a Raman spectrum was found to be albite. The spectra of the two components of the gemstone are presented in Fig. 6.

4. Raman Analysis on Stones Set in a Reliquary Cross from the Basel Cathedral

Only rarely does a gemologist get the opportunity to investigate the stones adorning historical items. The investigations of Meixner [14], CISGEM [15], Bosshart [16], Köseoglu [17], Querré et al. [18], Bouquillon et al. [19], Querré et al. [20], and Scarratt [21] are notable exceptions. The prudence and concern of museum curators is undoubtedly a major reason why so many important historical and religious pieces of jewelry lack precise descriptions of their materials. However, the scarcity of both analytical techniques and research organizations specialized in nondestructive methods may be the primary reason

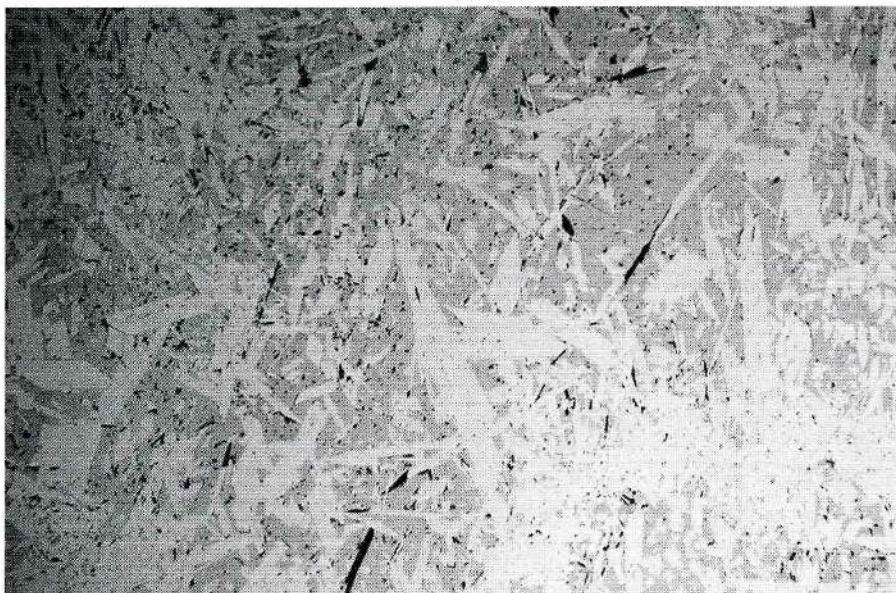


Figure 5 A dark violet jade cabochon revealed its complex nature under the microscope in reflected light. The darker mineral groundmass was found to be albite feldspar; the lighter crystals are jadeite.

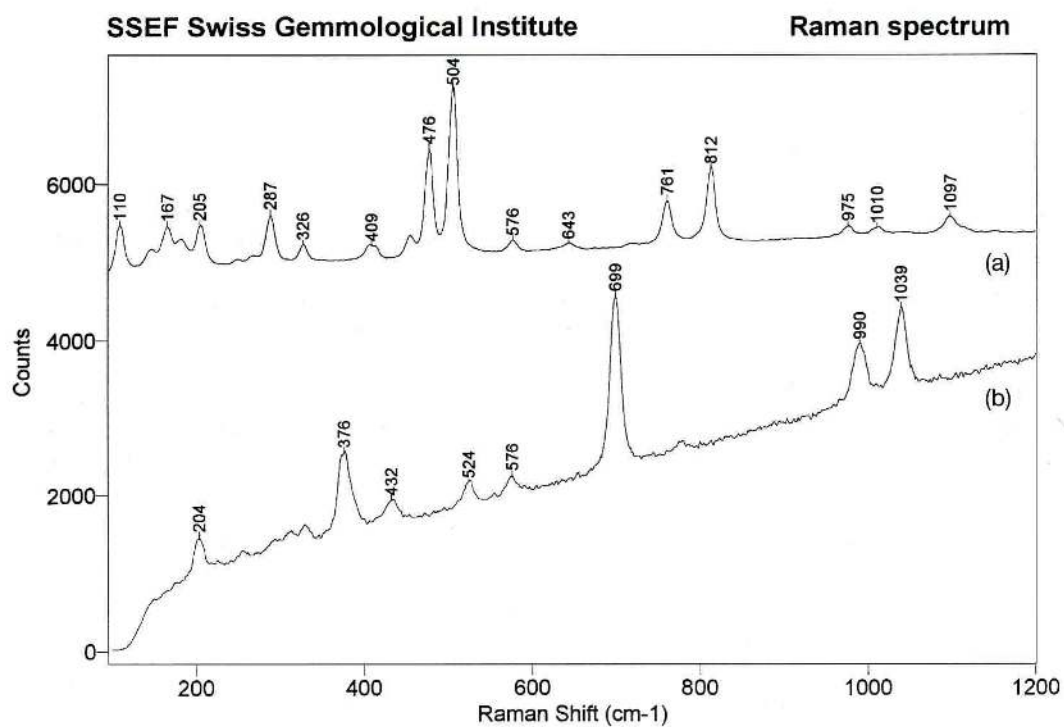


Figure 6 Raman spectra of (a) albite and (b) jadeite found in a dark violet jade cabochon.

for so many vague descriptions of the materials used in such objects. The Louvre Museum in Paris is one of relatively few repositories that have a well-equipped analytical laboratory; at the Louvre, microprobes are used to investigate a wide variety of very delicate, rare, historical objects [20].

Two religious artifacts of the Gothic period (1250–1520)—a reliquary cross 37 cm high and a monstrance 55 cm high—were investigated in collaboration with the Historical Museum of Basel, Switzerland. Such unique objects should, of course, be tested only by techniques that ensure no risk of damage. The position of the set stones as well as the delicate nature of the pieces together with their size inhibit the application of a refractometer. Therefore, Raman spectroscopy together with a microscopic investigation is the most adequate method of analysis, although handling of the objects is still difficult.

To be able to handle such large objects, the table of the microscope has to be dismounted so they fit under the microscope stage. These valuable pieces should preferably rest on several layers of foam rubber, according to the desired height. Then, the area of analysis has to be chosen and very often it is necessary to hold the object in the right position manually. Good results can, however, still be obtained, as shown in our example.

The stones used to adorn these pieces are mounted in metal settings which are attached at various places on the items. This also inhibits the use of classical gemmological means such as measuring the refractive index of the stone. Both pieces were a surprise, as they contained a high number of assembled stones, doublets, and glass. Some of the stones were cut as cameos. Among the natural stones in the reliquary cross and the Dorothy monstrance, several varieties of quartz (rock crystal, amethyst, citrine, agate, and black chalcedony) were encountered. Other natural gemstones were comprised of peridot, garnet, sapphire, spinel, and turquoise (Fig. 7).

Both pieces also contained quartz-topped doublets. However, whereas the stones in the reliquary cross had a red color due to red pigment in the cement layer, the doublets in the Dorothy monstrance are colorless. Because there is no reason to make colorless doublets out of an already colorless material, it is likely that the pigment used here faded over the centuries. For a more complete description of these objects, see Ref. 11.

B. Analysis of Internal Features (Inclusions)

Solid inclusions in gemstones are an important proof of the authenticity of a stone and the identification of such inclusions is helpful in origin determinations of gemstones. When they reach the surface, it is easy to perform a chemical analysis using the electron microprobe. In most cases, however, inclusions are within the gemstone, and it is only by observation and comparison with already analyzed inclusions that a determination is possible. Micro-Raman spectroscopy, however, allows a destruction-free identification of foreign materials below the surface. Analysis of inclusions not reaching the surface is possible down to a depth of 5 mm, but best results are obtained when the inclusion is close to the surface of the stone and perpendicular to the laser beam.

1. Raman Analysis of Inclusions in Corundum for Origin Determination

For sapphires, it is sometimes very hard to distinguish stones which have a Sri Lankan origin from those from Kashmir. The difference in commercial value, however, is considerable. Stones from both sources may have overlapping properties such as fine rutile particles along growth layers or as fine dust lines, healing fissures, and mineral inclusions. Unique to Kashmir sapphires are, however, two types of mineral inclusions, one being tourmaline and the other pargasite in the form of elongated crystals [22]. Pargasite has a

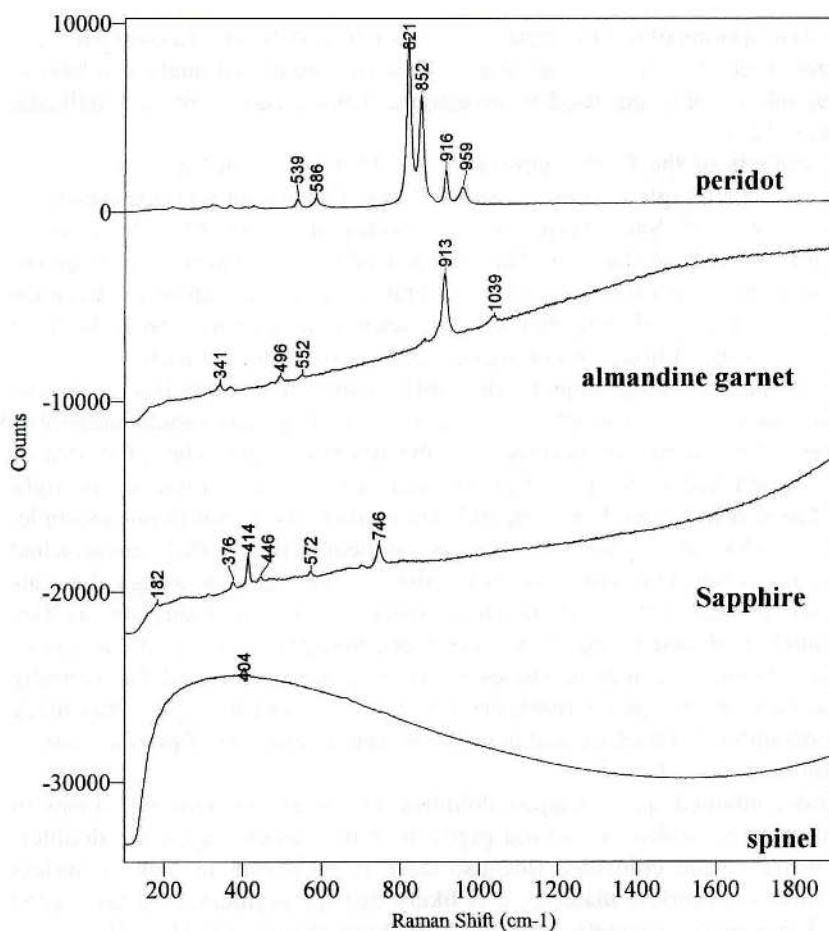


Figure 7 Raman spectra of four gemstones identified in the Dorothy monstrance, a reliquary of the Basel cathedral from the 15th century.

distinctive Raman spectrum which shows even if the crystal is not cut on the surface (Fig. 8); hence, the origin of the stone can be determined.

A relatively new source of sapphires is Madagascar. Stones from this occurrence have partly overlapping properties to those from Sri Lanka and Kashmir [23]. In addition, several mineral inclusions such as apatite, zircon, and calcite, three-phase inclusions consisting of a liquid and gaseous phase of CO_2 and diaspore as the solid phase (Fig. 9) could be identified. Three-phase inclusions with such a composition have so far only been observed in sapphires from Sri Lanka, thus ruling out Kashmir as possible source.

2. Raman Analysis of Gemstones Behind Plastic or Glass

The identification of diamond is most easily done with a thermal probe (thermotester). It seems, however, impossible to identify the nature of diamond-looking stones set in a wristwatch under the watch glass [10]. With a Raman microscope, it is sufficient to focus the laser beam down through the "glass" and on the supposed diamonds. The resulting Raman spectrum recorded is a combined spectrum of the "glass" material and the dia-

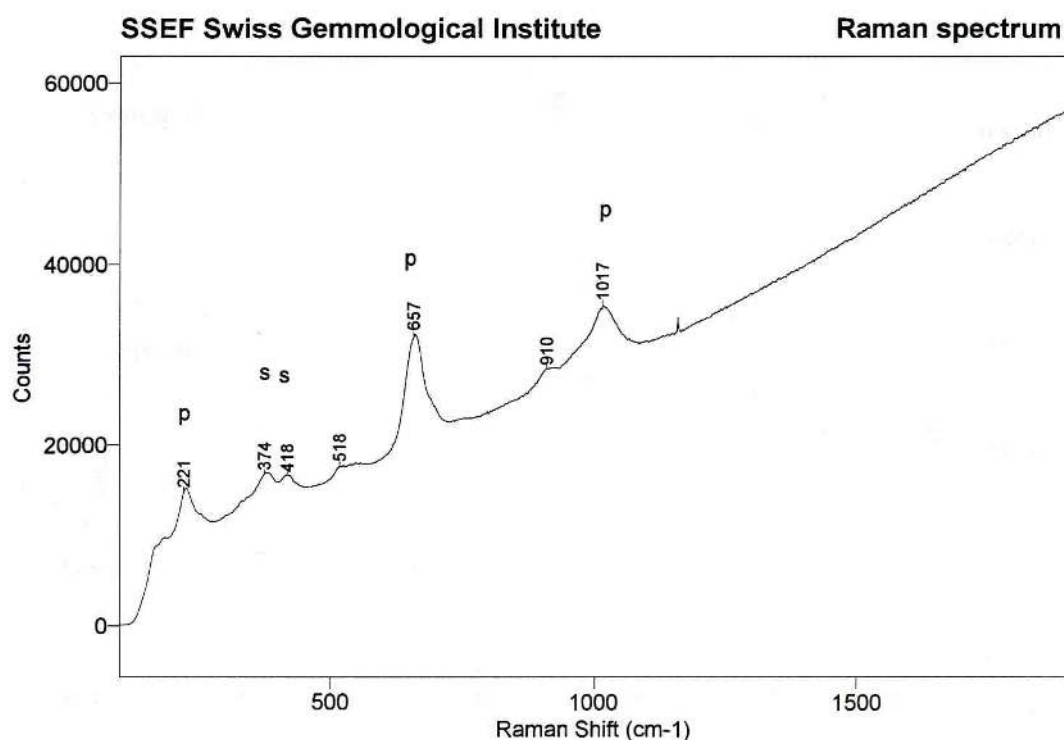


Figure 8 Raman spectrum of a pargasite inclusion in a sapphire from Kashmir. Note that the peaks with a “P” belong to the pargasite spectrum, whereas the peaks with a “s” belong to the spectrum of the sapphire host.

mond. Other applications of Raman spectroscopy to verify the authenticity of diamonds or other gemstones is when they are sealed in plastic boxes or embedded in epoxy resin, as shown in Fig. 10. A test with the Raman spectrometer through the plastic quickly identifies the gemstone. The sample diagram in Fig. 11 shows the Raman characteristics of diamond (1332 cm^{-1}) through the epoxy layer (major peak at 1606 cm^{-1}).

C. Gemstone Treatments

An important field in gemmology is the determination of gemstone treatments to enhance their appearance. These treatments range from heating the stones to improve their color, filling fissures or impregnating stones with colorless substances to improve their clarity and color, to dyeing. Some of these treatments are accepted by the trade; others are not.

1. Raman Analysis of Impregnated Jadeite

Waxes and resins are commonly applied to impregnate jade for richer color and more stability. Conventionally, the distinction between A-jade (not treated), B-jade (impregnated with colorless substances), and C-jade (impregnated with colored substances) is carried out with infrared spectroscopy. The Raman spectrometer does, however, also show peaks in the characteristic areas for organic substances when analyzing impregnated jade (Fig. 12). Here, it is important that sufficient material is available. Therefore, it is best if the analysis can be performed in a filled cavity.

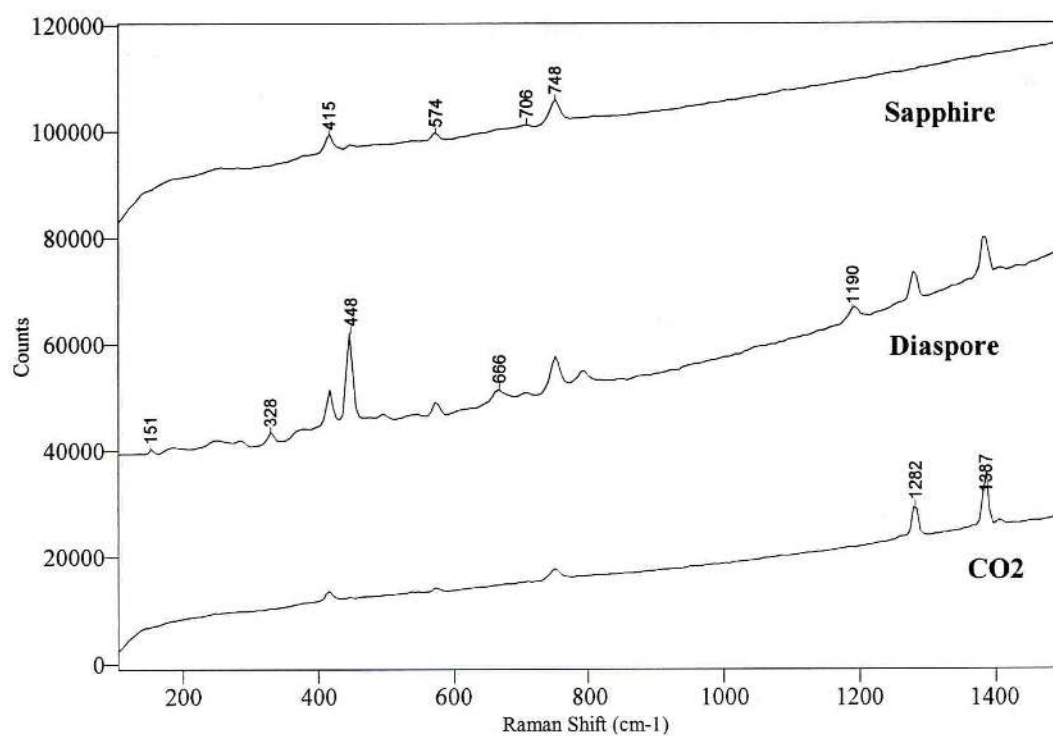


Figure 9 Raman spectrum showing the different phases of a three-phase inclusion in sapphire from Madagascar. The labeled peaks are assigned to sapphire (top), diaspore (middle), and CO₂ (bottom).

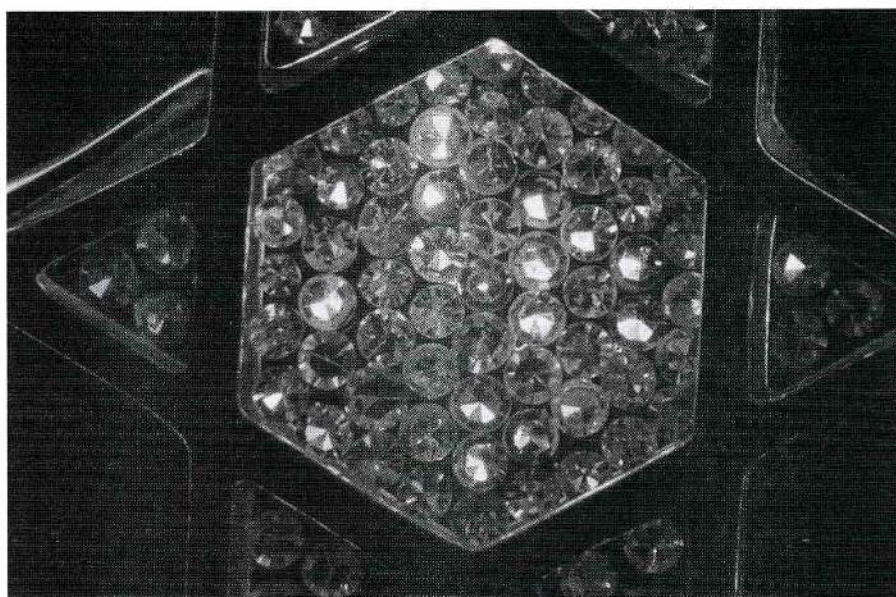


Figure 10 David's star, composed of diamonds embedded in epoxy resin.

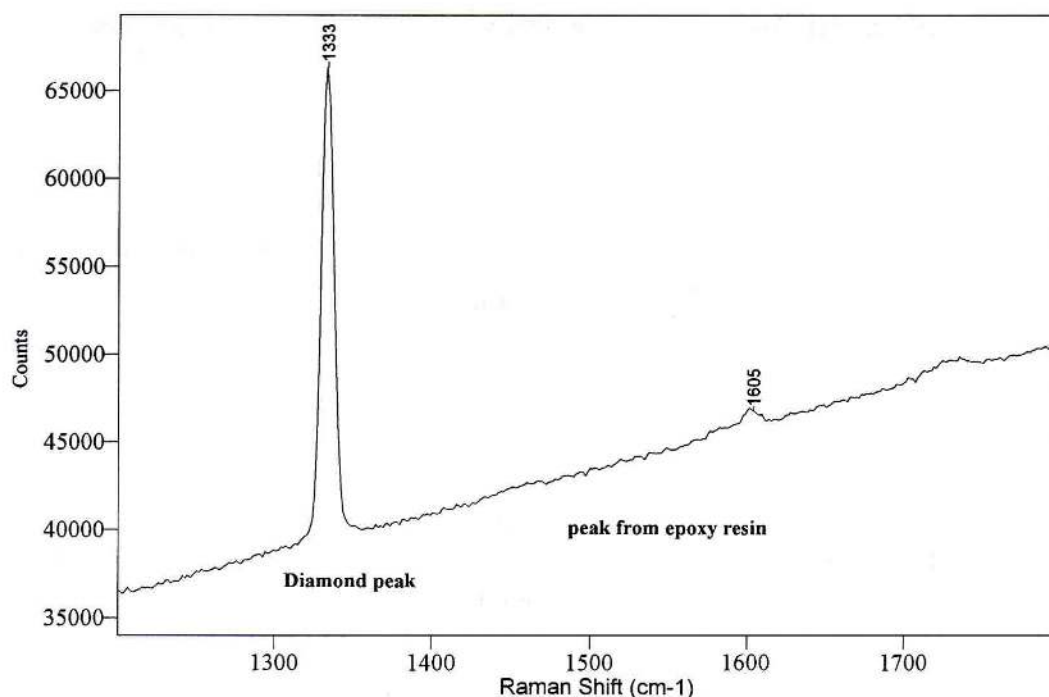


Figure 11 Raman spectrum of one of the diamonds in the David's star, showing the diamond peak and a peak from the epoxy resin.

2. Raman Analysis of Dyed Quartzite to Imitate Jadeite

A strand of light green beads, submitted to the laboratory as jadeite, proved to be dyed quartz (Fig. 13). The Raman spectra of quartz and jadeite are significantly different so that a distinction between the two can easily be performed (Figs. 12 and 14). Quartz may contain the mica Fuchsite to give it a green color (so-called aventurine quartz), but this example showed the color concentration along grain boundaries and fissures. In Fig. 14, the spectrum of quartz and the spectrum of the green dye are given.

3. Raman Analysis of Artificially Colored Pearls

The treatment of pearls is not a new problem which the gemmologist has to face. For decades, pearls have been immersed in silver nitrate to give them a black color. Usually, there is enough silver nitrate in the pearl to detect it on x-radiographs. It may, however, also be determined by Raman spectroscopy. Pearls dyed with silver nitrate show a distinct peak at approximately 240 cm^{-1} , which is not present in natural black pearls (Fig. 15). Lately, the irradiation of pearls as well as using organic dyes is more and more common. Here, Raman spectroscopy may also prove to be of invaluable help, because, generally, black pearls of natural coloration show a lower aragonite peak than artificially colored black pearls. A study on this subject using the fresh nacre from shells as references is still in progress.

4. Raman Analysis of Fissure Fillers in Emerald

The clarity of an emerald is reduced by the presence of inclusions—guest crystals, negative crystals, healing fissures, structural features, and open fissures. Open fissures are especially

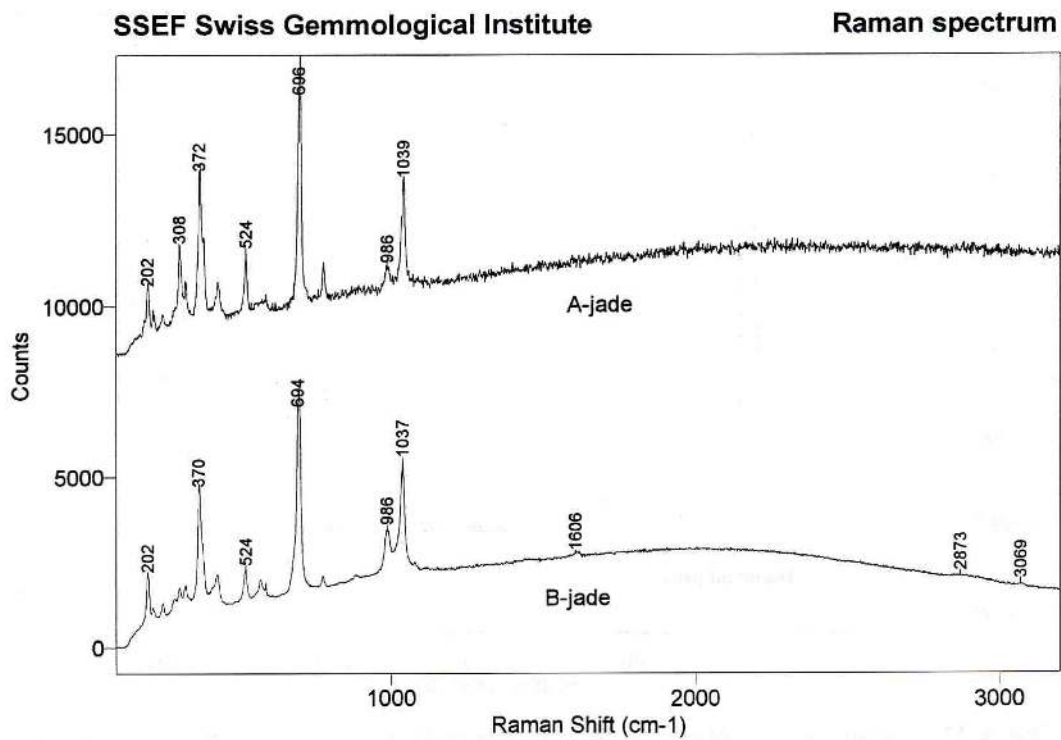


Figure 12 Raman spectra of untreated jadeite (A-jade, top) and jadeite impregnated with colorless epoxy resin (B-jade, bottom). The Raman spectrum at the bottom shows, in addition to the jadeite peaks, weak peaks belonging to the epoxy resin.

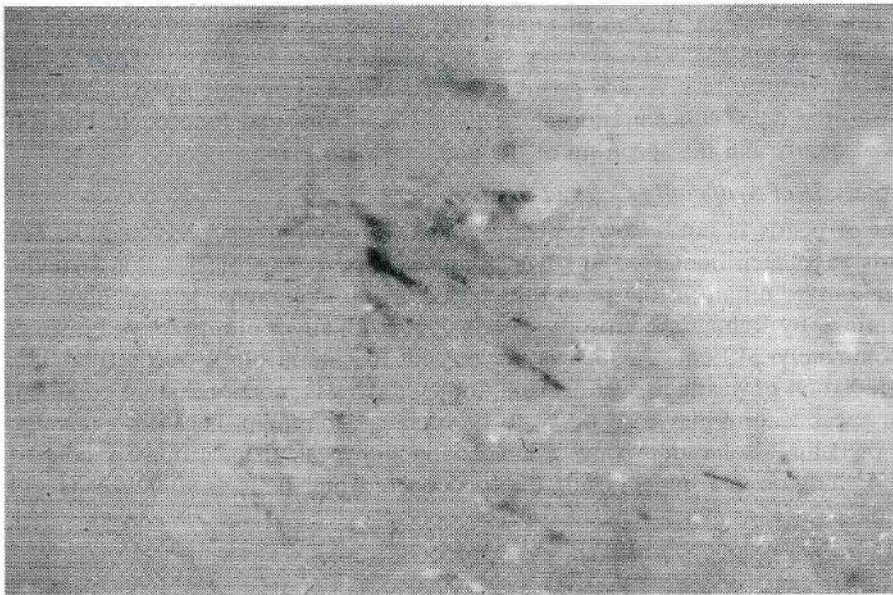


Figure 13 Green dye in a white quartzite as jadeite imitation.

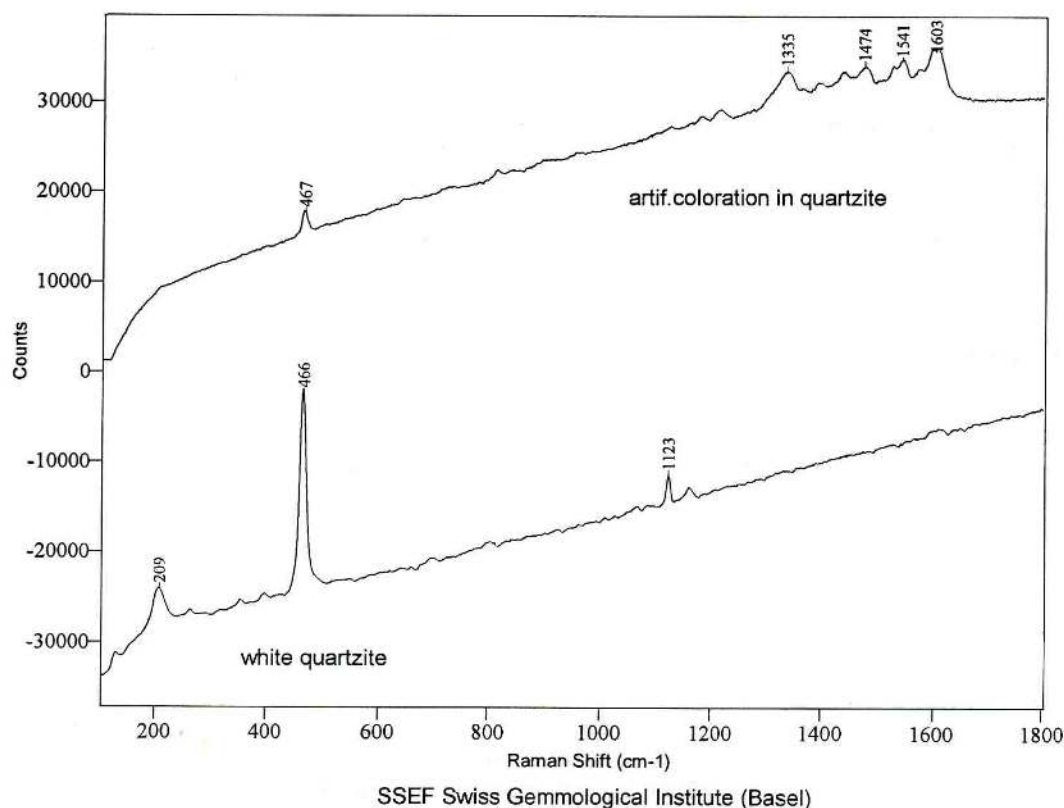


Figure 14 Raman spectra of the white area of the quartzite showing only peaks related to quartz (bottom) and the green artificial coloration (top).

clearly visible in Colombian emeralds because of their reflection, because the stones often are otherwise quite clean. In emeralds from other origins (Brazil, Russia, Zambia, Zimbabwe–Sandawana, Afghanistan, India, etc.), crystalline inclusions are more frequent, but fissures are still present [24–28].

To improve the apparent lower clarity of emerald, fissures may be hidden by impregnating the stones with some more or less permanent colorless substances. Although colored oils and resins are also used to fill emeralds, these materials are not covered here. Effective fillers have refractive properties close to that of emerald. Such substances comprise oils (natural or synthetic), resins (natural or on the basis of natural resins), as well as glues or artificial resins. Fissure treatments have been practiced for a long time, and mention of these treatments reach back to Plinian times [29–38]. The identification of the nature of filler substances in emeralds started to become an issue when artificial resins, commonly epoxy resins, were used as fissure-filling substances. These substances are commercially available or consist of a mixture of commercially available substances. Therefore, their properties are well known and spectra readily available [39].

As in FTIR spectroscopy, oils and resins show different peaks depending on their chemical composition. Of all analyzed oils, a distinction could be made between two

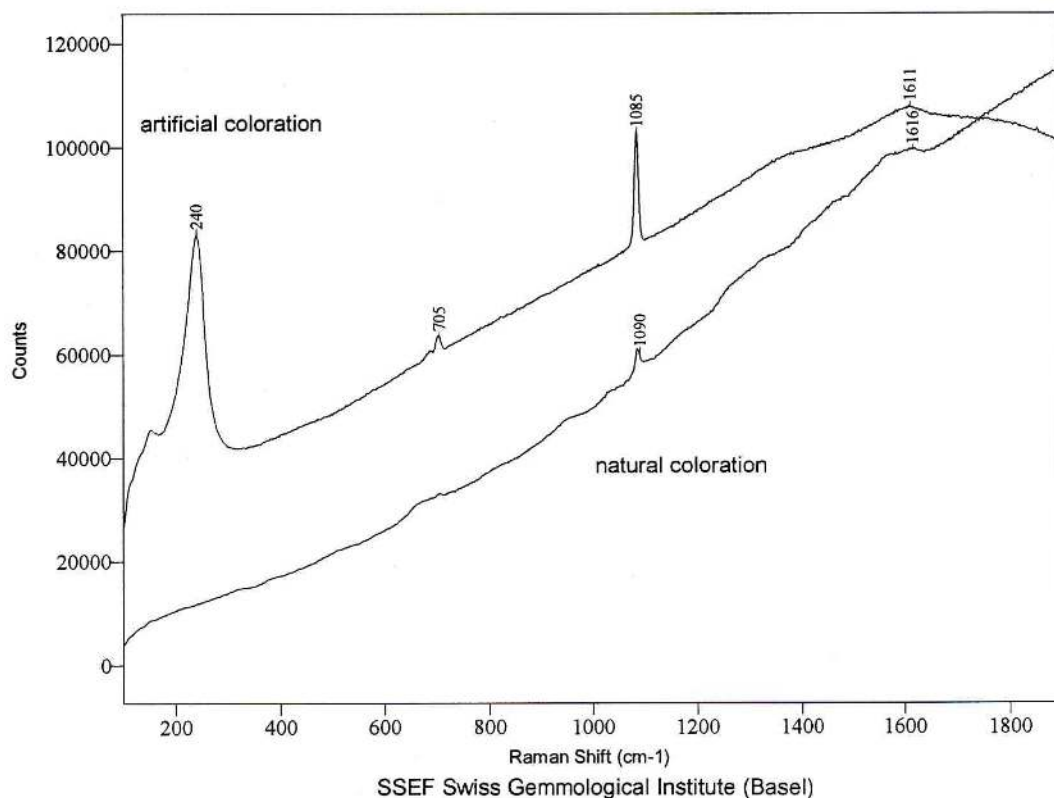


Figure 15 Raman spectrum of a dyed black cultured pearl (top) and a black cultured pearl of natural coloration (bottom). The strong peak at 240 cm^{-1} indicates an artificial coloration by silver nitrate.

different types of oil: One type primarily includes oils such as mineral and paraffin oil (Fig. 16). The other type of oil is cedar wood oil, which can be natural or produced synthetically. The various cedar wood oils tested in the laboratory have some variations in peak intensity, probably due to aging and oxidation. Their major peaks in the lower region of wave numbers at 1441 cm^{-1} , 1455 cm^{-1} , and 1666 cm^{-1} generally occur in all tested samples (Fig. 16).

One organic substance which currently is rarely used to fill emerald fissures is Canada balsam. This substance is accepted in the trade as emerald filler because it reveals chemical properties similar to the oils; that is, it does not polymerize like epoxy resins do. The main properties of these substances are their inability to polymerize. Therefore, Canada balsam does not harden as much as epoxy resins do and is generally easier to remove from the stone if it starts decomposing.

The various epoxy resins marketed under the names Opticon, Palma, and Epon 828 have identical spectra with major peaks distinguishing them from the other substances mentioned earlier (Fig. 17). One newer substance differs slightly from the above mentioned epoxy resins. This substance called Permasafe was made available in a solid state and was identified as yet another artificial resin of the bisphenole A family (Fig. 17).

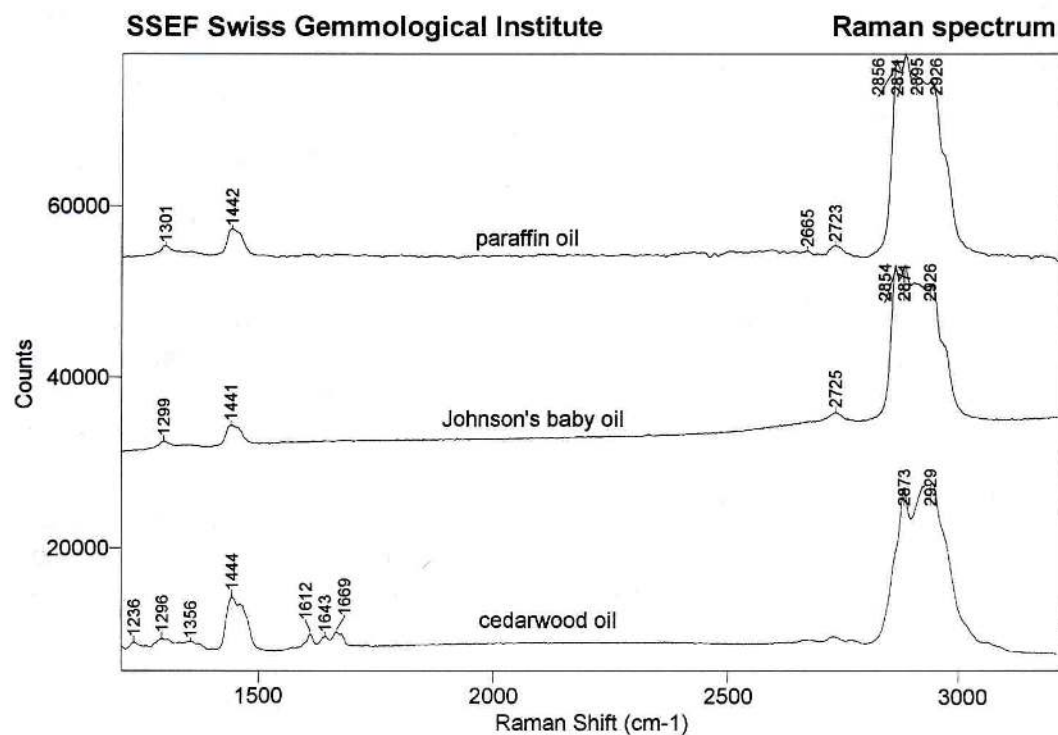


Figure 16 Raman spectrum of paraffin oil, Johnson's Baby Oil, and cedar wood oil.

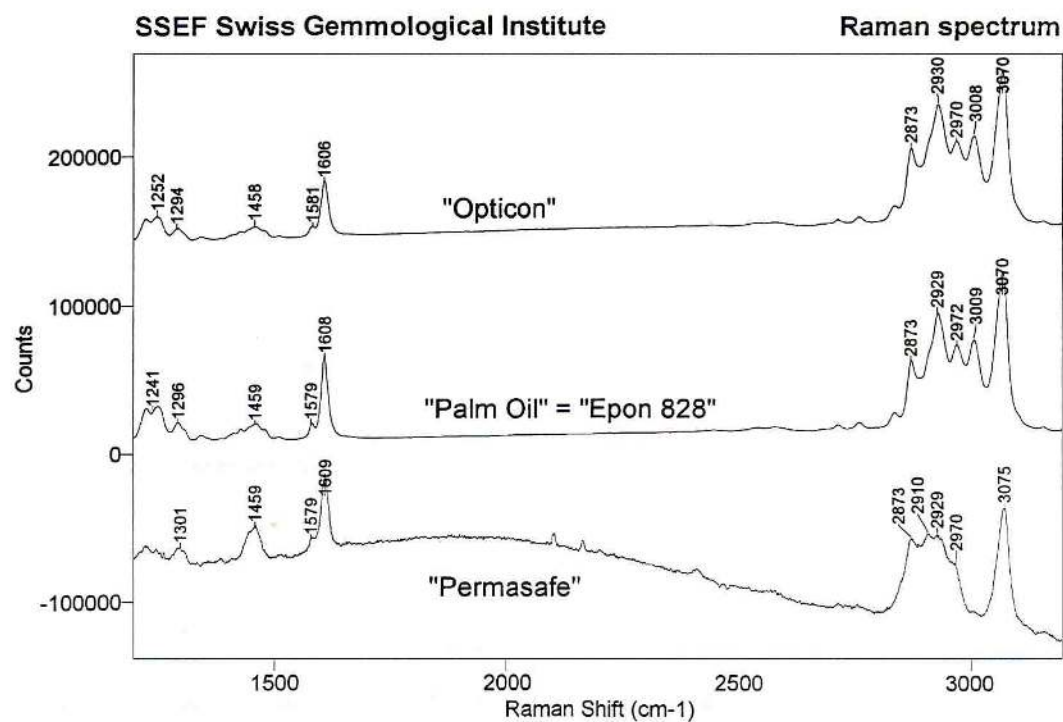


Figure 17 Raman spectrum of Opticon (a), Palm Oil (b), and Permasafe (c).

The spectra presented in Figs. 16 and 17 show that a distinction can be made among various emerald filler substances. Other materials such as hardeners for epoxy resin or various polishing materials (diamond powder, chromium oxide) also show distinct peak positions.

Fissure fillers have two characteristic Raman spectroscopic areas, which do not interfere with the emerald spectrum: 1200–1700 cm^{-1} (Fig. 18) and 2800–3100 cm^{-1} . The major Raman spectroscopic area for emerald lies between 100 and 1100 cm^{-1} . The second area, although it displays more intense peaks than the first, may, however, be masked by a strong Raman fluorescence of the emerald. Therefore, when conducting a Raman spectroscopic analysis on emerald fillers, more emphasis should be given to the analytical area between 1200 and 1800 cm^{-1} . In this area, interference with the emerald spectrum is minimized and good spectra of fissure fillers are obtained (Fig. 18).

Storage of the obtained spectra in a reference library file is advisable, so that the spectra of fillers found in emeralds can easily be compared. It is also of advantage to analyze the whole possible Raman spectral range of the substance between 200 and 4000 cm^{-1} , but to save the spectra in the range used for detecting fissure fillings in emerald as well.

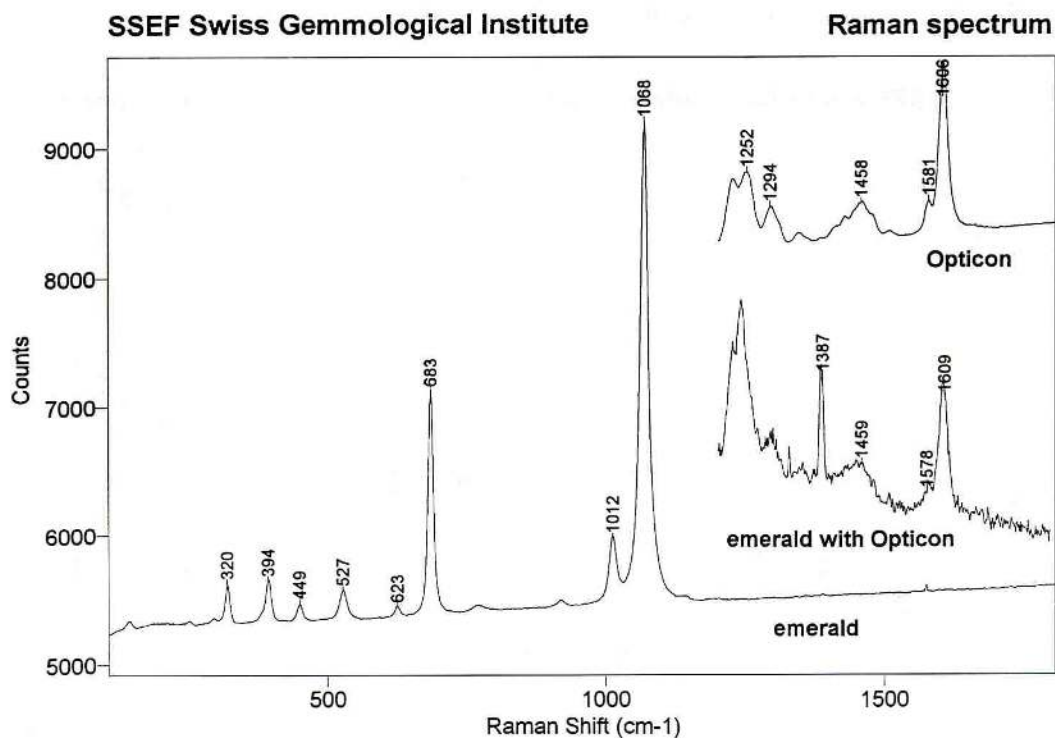


Figure 18 Raman spectra of Opticon epoxy resin (top), of emerald without treatment (bottom), and of an Opticon treated emerald (middle). The valuable peaks in this figure are in the 1200–1800- cm^{-1} area, where the vibrations of organic fillers are visible.

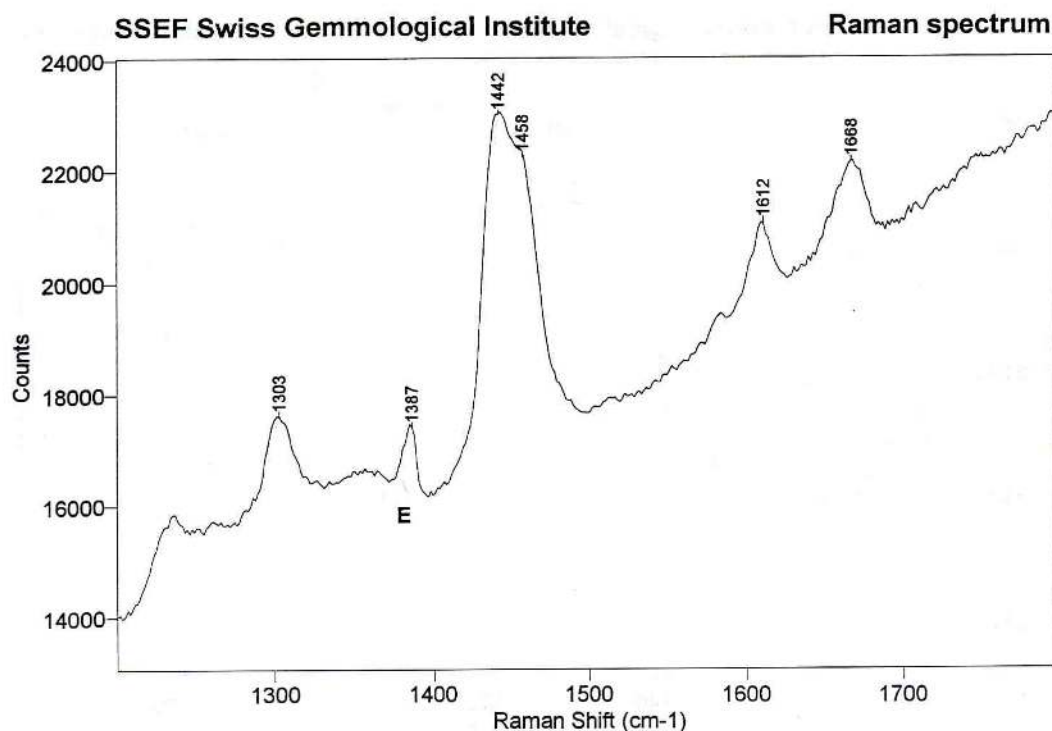


Figure 19 Raman spectrum of an emerald fissure with cedar wood oil.

Figure 18 shows, besides the Raman spectrum of an emerald, the spectrum of a typical epoxy resin—in this case, Opticon. When an epoxy resin is encountered in an emerald fissure, the spectrum may vary from a strong signal to a very weak outline of the major peak. The major epoxy peak at 1606 cm^{-1} is, however, always visible to a certain degree. In contrast, emeralds filled with cedar wood oil show a different spectrum (Fig. 19).

Mixtures of various substances are generally also identifiable. Raman spectra of the new type of treatment from the United States called "Gemmatrat" showed that it possesses spectroscopic properties of a mixture of artificial resin and oil. Multiple treatments which may be caused by incomplete cleaning and refilling with another substance end up in a similar mixed substance spectrum (Fig. 20). For a more detailed description on the identification of fissure fillers in emerald, see also Ref. 39.

IV. FUTURE OUTLOOK

The above-described examples are applications presently performed in major gemmological laboratories. As Raman microspectrometry is a relatively new method in gemmology, all possibilities of gemstone detection are probably not exhausted yet. With new gemstone treatments such as the treatment of color in diamond, a rising awareness of those treatments in the gemstone trade, and smaller and more affordable instruments, it is safe to assume that a Raman microspectrometer will soon be a standard instrument in all major gemmological laboratories.

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