A Raman microscope in the gemmological laboratory: first experiences of application

Prof. Dr Henry A. Hänni, Dr Lore Kiefert and Jean-Pierre Chalain

SSEF Swiss Gemmological Institute, Basel, Switzerland

Dr Ian C. Wilcock

Renishaw plc, Old Town, Wotton-under-Edge, Glos, GL12 7DH

ABSTRACT: Various applications of Raman spectroscopy in a gemmological laboratory are discussed with examples. The major advantage of this system over classical methods of gem testing is the non-destructive identification of inclusions in gemstones and the determination of organic fracture fillings in emeralds. Also, quick and precise identification of gemstones unmounted or in jewellery, as well as the non-destructive analysis of archaeological samples are possible. Due to the high resolution of the instrument, several phases in a gemstone can be identified. Limitations of the Raman microprobe are also listed.

Keywords: Raman spectroscopy, inclusions, gemstone identification, fissure fillings, archeometry

Introduction

The Raman effect was discovered by the Indian physicist Sir C.V. Raman at the beginning of this century. He observed that molecules which were hit by a monochromatic light beam scattered the light and produced spectra which were characteristic for different materials. Although Raman spectroscopy has so far not been widely known in the study of gemstones, it was introduced as an analytical tool for minerals a long time ago. Raman spectroscopy is also well established in other areas of application, such as physical chemistry, materials science, and superconductor and semiconductor physics.

Raman spectrometers have traditionally been large and very expensive instruments, but recent technical developments have revolutionized this technique. The traditional, rather insensitive instruments can be replaced by modern, compact, highly sensitive, easy-to-use and flexible instruments, more suited to the gemmological laboratory (see, for example, Williams *et al.*, 1994). A typical instrument consists of a classical microscope with either transmitted or reflected light, a low-power laser excitation source, the spectrometer for high resolution light analysis and an appropriate computer for data collection and analysis. The total system fits easily on a desk top *(Figure 1)*. For these reasons, Raman microscopes are gradually becoming more widespread in gemmological laboratories around the world, among them the University of Science and Technology in Nantes, AIGS Bangkok, and CISGEM Milan.

The Raman microscope presents the gemmologist with a unique combination of

 ISSN: 1355–4565

properties which make it a useful additional technique in tackling gemmological problems. These properties include a high spatial resolution, as low as one micrometre, allowing the highly accurate positioning of the microscope to study inclusions as small as one micrometre. With a high-power objective and spatial light filtering in the spectrometer, the system can be 'confocal', allowing the operator to construct profiles of layered compounds or inclusions inside gemstones, with minimal contribution from the main bulk species. In addition, the analysis is rapid, requires no sample preparation and, most importantly, is non-destructive.

The Raman microscope can thus provide spectra typical of the analysed materials. These spectra can be identified by comparison with known spectra, which means that a large set of reference spectra is an important condition for the successful use of the method.

The following references are generally recommended for understanding the method (McMillan and Hofmeister, 1988; McMillan, 1989); for its mineralogical (Griffin, 1987; Smith, 1987; Malézieux, 1990) and for its gemmological applications (Dhamelincourt and Schubnel, 1977; Delé-Dubois *et al.*, 1980; Delé-Dubois *et al.*, 1981; Delé-Dubois and Merlin, 1986; Pinet *et al.*, 1992; Schubnel, 1992; Lasnier, 1995) should be consulted.

Experimental and technical background

Most gemmologists are familiar with visible spectroscopy, i.e. from an incident broad band white light source, characteristic wavelengths or energies are absorbed by chromophore elements such as chromium in ruby. Fewer are familiar with emission spectroscopy and its application, for example, in X-ray fluorescence. Here the incident energy excites electrons in the substrate, which then decay back to the ground state, *emitting* distinct wavelengths of light, allowing the identification of chemical elements in the substrate (Stern and Hänni, 1982; Hänni, 1993).

The Raman effect is, in contrast, a scattering technique in which a monochromatic light source is used (usually a visible laser). Whilst most of the light is simply scattered and contains no useful information (the so-called Rayleigh or elastic scattering), a small amount, typically one photon in 10^6–10^8, is re-emitted having lost some energy. This shifted or Stokes radiation appears as lines in a spectrum characteristic for the substance under study. Most materials that the gemmologist or mineralogist will encounter have a typical Raman spectrum, serving as a 'fingerprint' for that type of material. The only major subset of materials that cannot be studied are metals and alloys. In addition, subtle changes within one material such as alterations in crystallinity and composition can often be detected.

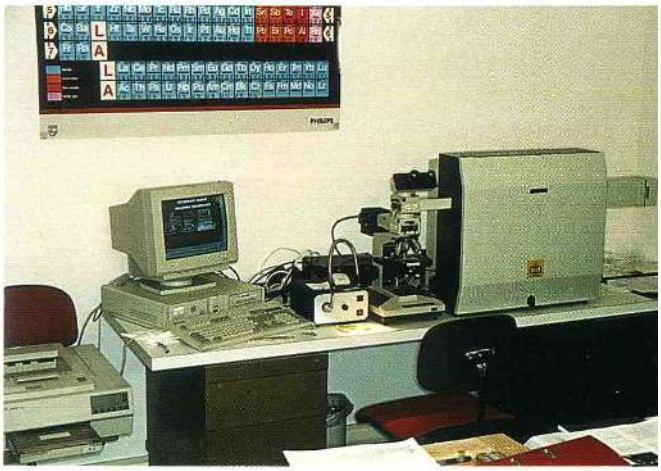


Figure 1: *A Renishaw Raman microscope installed on a laboratory table at SSEF. The laser source is situated behind the spectrometer body.*

The Raman studies presented here were performed using a Renishaw Raman System 1000 equipped with a Peltier cooled CCD detector, together with a 25 mW air-cooled argon ion laser (Omnichrome) lasing at 514 nm *(Figure 1)*. The laser light was focused on to the sample and the scattering collected with an Olympus BH series microscope equipped with x10, x20 and x50 MSPlan objectives.

Using the 'extended scanning' facility, a complete spectrum from 100 up to 9000 cm^{-1} could be measured with a resolution of

Table I: Section of a Swiss Gemmological Institute search file for minerals with Raman peaks in order of the peak intensities. Line 101 shows the figures related to the mineral bustamite (peaks measured in cm^{-1})

	Colour	Group	Mineral	1st Peak	2nd Peak	3rd Peak	4th Peak	5th Peak	Reference	Notes
95			Brochantite	971.4	1074.5	594.3	480.7	386.5	SSEF	TSUMEB
96			Brookite	149.9					JNBM	USA p.222/514.5 nm 209.4s
97			Brookite	150.0	319.0				Schubnel	
98	Brownish-red		Brookite G	150.0	125.0	244.0	319.0	636.0	Maestrati	
99	Brownish-red		Brookite M	150.0	129.0	321.0	634.0		Maestrati	
100	Brownish-red		Brookite P	150.0	637.0	320.0	500.0	363.0	Maestrati	
101	Pinkish-brown		Bustamite	974.2	644.0	1036.5	315.1	405.4	SSEF	Franklin N.J. NMBS
102		Calcite	Calcite	1083.1	278.2	709.1	151.4	1433.1	JNBM	Mexico p.207/514.5 nm 19.9s
103		Calcite	Calcite	1084.0	279.0	709.0	152.0	1435.0	SSEF	Rough CH-Gonzen
104		Calcite	Calcite	1085.2	279.6				SSEF	3.05 ct

2 cm^{-1}. This allowed not just Raman measurements, but also simultaneous Raman and luminescence studies to be performed between 520 and 1000 nm. A standard PC computer with GRAMS/386™ software was used to collect and store the Raman spectra, as well as allowing data analysis, presentation and the ability to compare the collected data with reference spectra stored in a library in the memory.

Reference spectra

The identification of a mineral by Raman spectroscopy is a comparative method. Only in some rare cases is it possible to calculate and predict the peak positions of a given substance. Therefore the necessity of a collection or data base of reference spectra is extremely important. In the recent past some mineral data aimed at creating a comparison file have been published by the French scientists Maestrati (1989) Pinet *et al.* (1992), and Schubnel (1992). Renishaw is presently compiling a more comprehensive data base consisting of spectra supplied by the various users of their system. Meanwhile, the SSEF has developed its own preliminary data-base system with over 500 spectra from more than 200 different minerals using existing data and adding its own analyses. The reference samples analysed in the SSEF not only came mainly from the gemstone collection of one of the authors (HAH) but also from the Museum of Natural History in Basel (NMBS) and from other reliable collections. *Table I* shows an excerpt from the present SSEF search file. The spectra are not only in alphabetical order but also in order of the peaks, so that an unknown mineral can be identified by comparing the major peaks.

Examples of application

Solid inclusions in gemstones are an important indicator of the nature of a stone and may, additionally, be a characteristic feature of a particular origin. The identification of inclusions has been used frequently, among other methods, to determine the authenticity or origin of a stone. However, until recently the identification could in practical terms only be carried out when the inclusion reached the surface of the stone. 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. *Figure 2a* shows zircon clusters in a sapphire from Burma; *Figure 2b* shows the Raman spectrum of one of these inclusions, which was easily identified using the search file. An invaluable feature of Raman spectroscopy is that the analysis of solid inclusions can be carried out without damage to the gemstone.

The study of *fluid inclusions* in gemstones is of importance for the determination of the true identity of crystals. The phase transitions of fluids, i.e. the determination of the freezing and melting point of fluid inclusions, can be controlled under a microscope with a cooling/heating stage. This method, commonly applied with thin sections is called microthermometry. Peretti *et al.* (1990) have modelled the pressure oscillation during the formation of Kashmir sapphires using this method. Bruder (1995) has investigated fluid inclusions in sapphires and rubies from different origins. He found that primary and pseudo-secondary fluids in sapphires consist of pure CO_2. During his investigations on ruby samples, Bruder found characteristic differences among the compositions and densities of the fluids. He found indications that fluids in rubies from some marble deposits (e.g. in Pakistan and Afghanistan) contain impure CO_2, the admixture most probably being H_2S. Such a mixture gives a characteristic Raman peak at 2011 cm^{-1} and is of importance for the origin determination of unheated rubies. Dubessy *et al.* (1989) have developed a

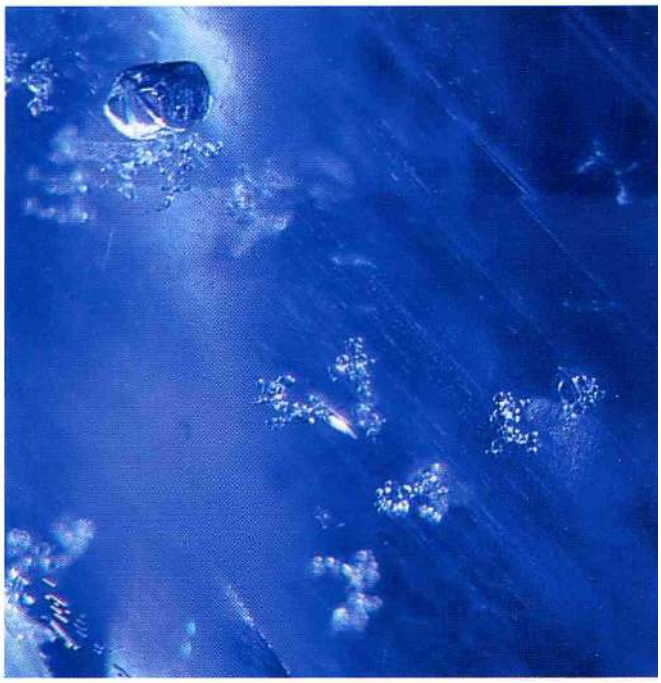
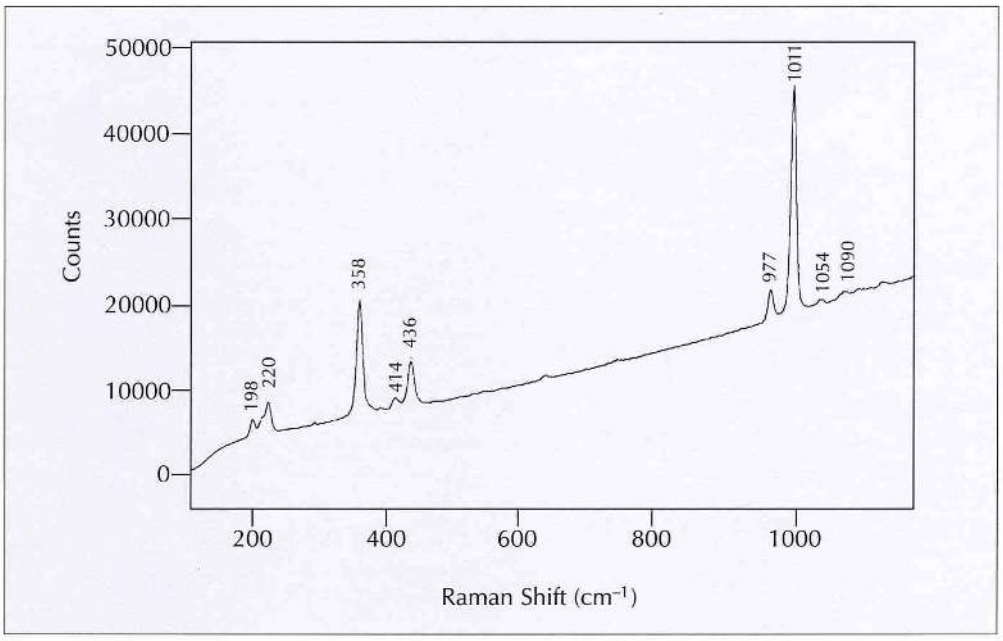


Figure 2a: *Zircon clusters in a sapphire from Burma, magnification 50x.*

Figure 2b: *Raman spectrum of zircon in a sapphire from Burma. The major peaks from zircon are at 1011, 358 and 436 cm^{-1}. The peak at 414 cm^{-1} belongs to sapphire.*



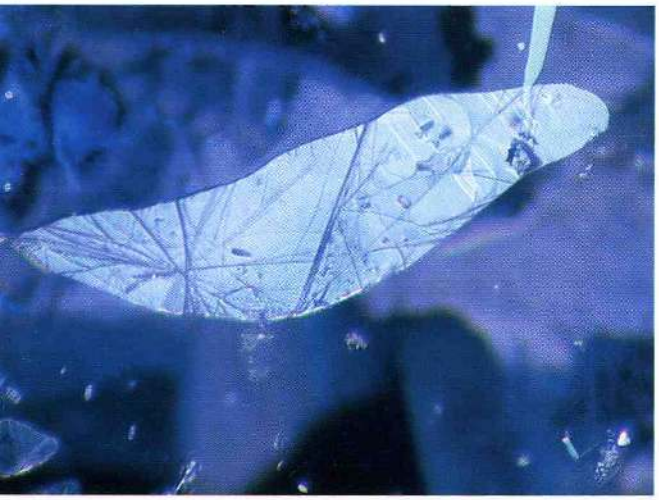


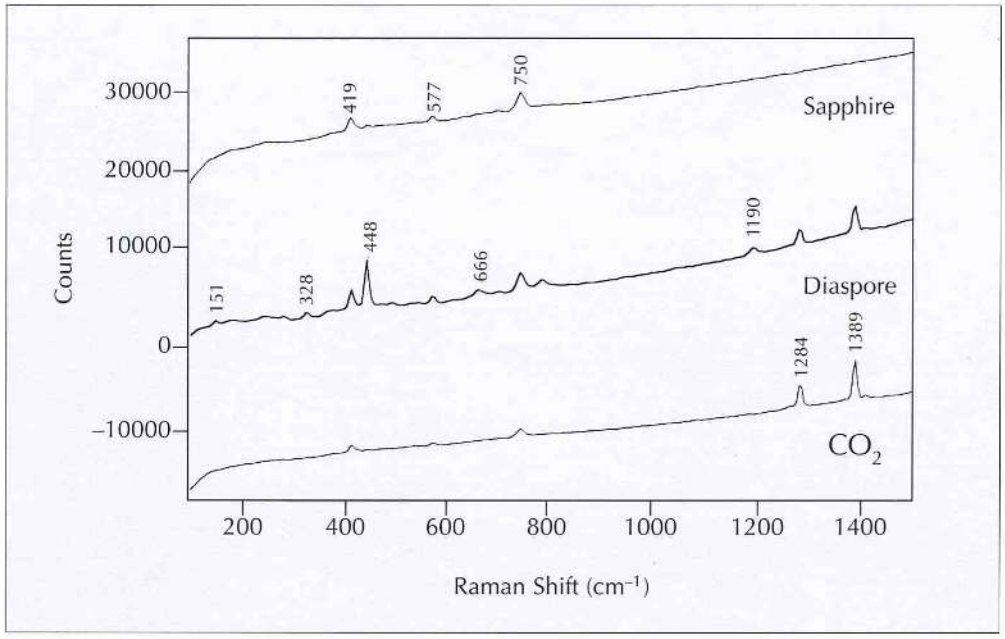
Figure 3a: *Three-phase inclusion in sapphire from Madagascar oriented parallel to the basal plane and showing liquid and gaseous CO_2 and diaspore needles. View parallel to the c-axis, magnification 50x.*

Figure 3b: *Raman spectrum showing the different phases of a three-phase inclusion in sapphire from Madagascar. The labelled peaks are assigned to corundum (top), diaspore (middle) and CO_2 (bottom).*

method of identification of mixed fluids using a program which quantitatively describes the composition of the fluids.

A *three-phase inclusion* in a sapphire from Andranondambo (south Madagascar) was an excellent candidate to evaluate the analytical possibilities with the Renishaw system (Kiefert *et al.*, 1996). *Figure 3a* shows a flat cavity in a tabular sapphire from Andranondambo. The microscope inspection revealed a gas bubble surrounded by a liquid phase containing bent fibrous crystals. The laser beam was directed on to these inclusions and the system produced the Raman spectra shown in *Figure 3b* which identifies corundum as the host, CO_2 and diaspore as inclusions.

The presence of carbon dioxide in fluids in corundum has been reported earlier (Koivula, 1980; Schmetzer and Medenbach, 1988; Bruder, 1995); its identification by Raman spectroscopy, however, is more straightforward than by microthermometry. The presence of a solid phase in CO_2 such as graphite or diaspore has been published in gemmological literature by Schmetzer and Medenbach (1988). Graphite was also identified by Raman spectroscopy in a three-phase inclusion in a sapphire from Sri Lanka.



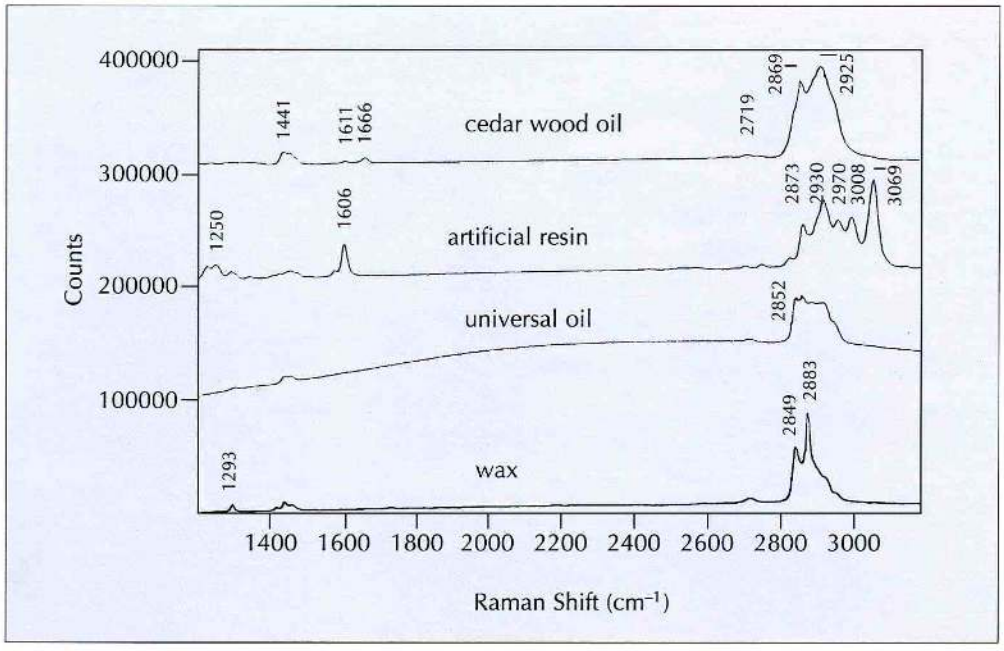
When produced by a flux technique synthetic stones may be identified by Raman spectroscopy by characteristic spectra from their included flux particles. A flux inclusion trapped in Chatham synthetic emerald produces its major Raman peaks at 221 and 570 cm^{-1}, while flux in a Douros synthetic ruby shows Raman peaks at 133, 824 and 850 cm^{-1}.

Organic fracture fillers in emerald frequently need to be identified for test reports. It is quite rare that an emerald is free of fractures and hence free of foreign material in fissures (Hänni, 1992). Organic substances such as oils and natural resins have been used for centuries as fissure fillers to enhance the clarity of emeralds. The organic substances have a refractive index close to that of emeralds and considerably reduce the reflection of fractures filled with air. The range of fillers encompasses numerous substances such as vegetable and mineral oils with volatile components, and more durable fillers like fats and resins (Hänni, 1992).

Nowadays, synthetic resins are used more frequently (Themelis, 1990) because they adhere more permanently to the stone than oils, and may not be released as easily due to their low solubility in detergents and solvents. However, the gem trade is sceptical about these synthetic resins for several reasons. One reason is that the use of artificial resins is relatively new and little is known about how they may alter with time.

The Raman microprobe enables a distinction between natural and artificial resins because of their different molecular structures. The Raman peaks for natural and artificial resin lie in two different parts of the spectrum, the first within the area between 2800 and 3100 cm^{-1}, a second area of characteristic but weaker peaks lies between 1200 and 1700 cm^{-1}. *Figure 4a* shows the Raman spectra of four different substances commonly used for filling fractures in emeralds. Peaks at 1250, 1606, 3008 and 3069 cm^{-1} are strong in artificial resins, but are absent or only very weak in natural resins and oils. Other differences lie within the intensities of certain peaks.

Figure 4a: *Raman spectra of organic substances commonly used to fill fractures in emeralds. The spectrum of the artificial resin, often referred to as 'opticon' in the trade, shows distinct differences from the other substances.*



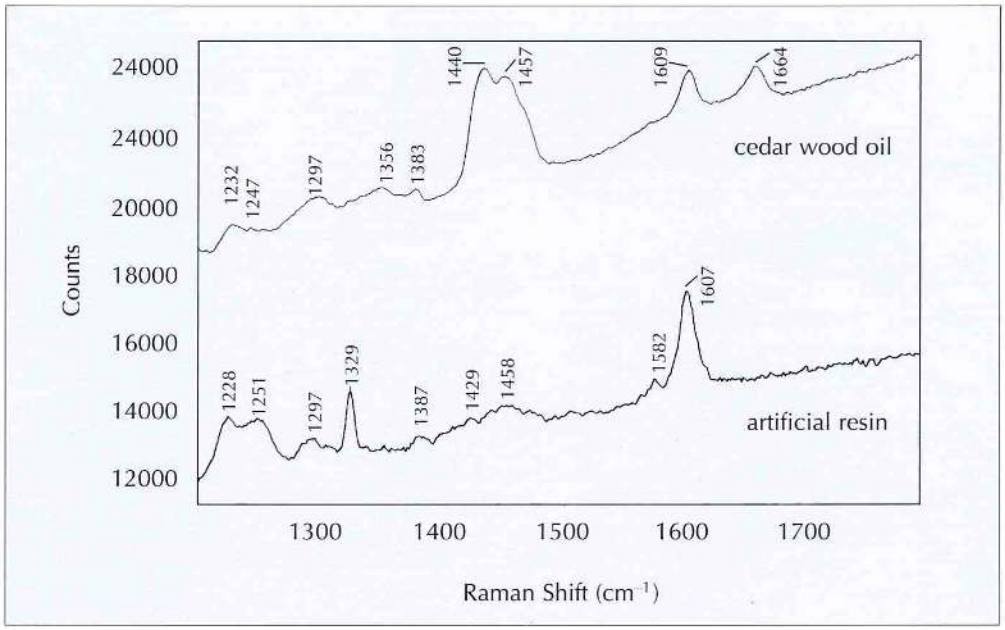


Figure 4b: *Raman spectra of two substances identified in fractures in emeralds.*

Figure 5a: *A watch with moving diamonds under a sapphire cover. By Raman microscopy it is possible to record the Raman line of diamond through the watch glass.*

After such resins have been introduced into emeralds, they may undergo alteration with time. Depending on the degree of alteration, the substance may display an increase in fluorescence which is superimposed on the Raman spectrum of fresh substances, especially in the 2800–3100 cm^{-1} area, so that the peaks in this area may hardly be visible. The 1200–1700 cm^{-1} area is less affected by this fluorescence, so that in some instances the peaks in this area are more useful for identification purposes. *Figure 4b* shows the Raman spectra of two fissure fillers detected in emeralds. The top spectrum shows a natural resin with strong 1440 and 1457 cm^{-1} peaks and an additional peak at 1664 cm^{-1} *(see also Figure 4a)*. In comparison, the artificial resin has much higher peak intensities at 1251 cm^{-1} and 1607 cm^{-1}, but much lower intensities in the 1450 cm^{-1} area *(see also Figure 4a)*. Hence, in this and in many other cases, the determination of the type of filler in an emerald fissure is possible.

The identification of diamond is most easily done with a thermal probe (thermotester) where direct contact between the instrument

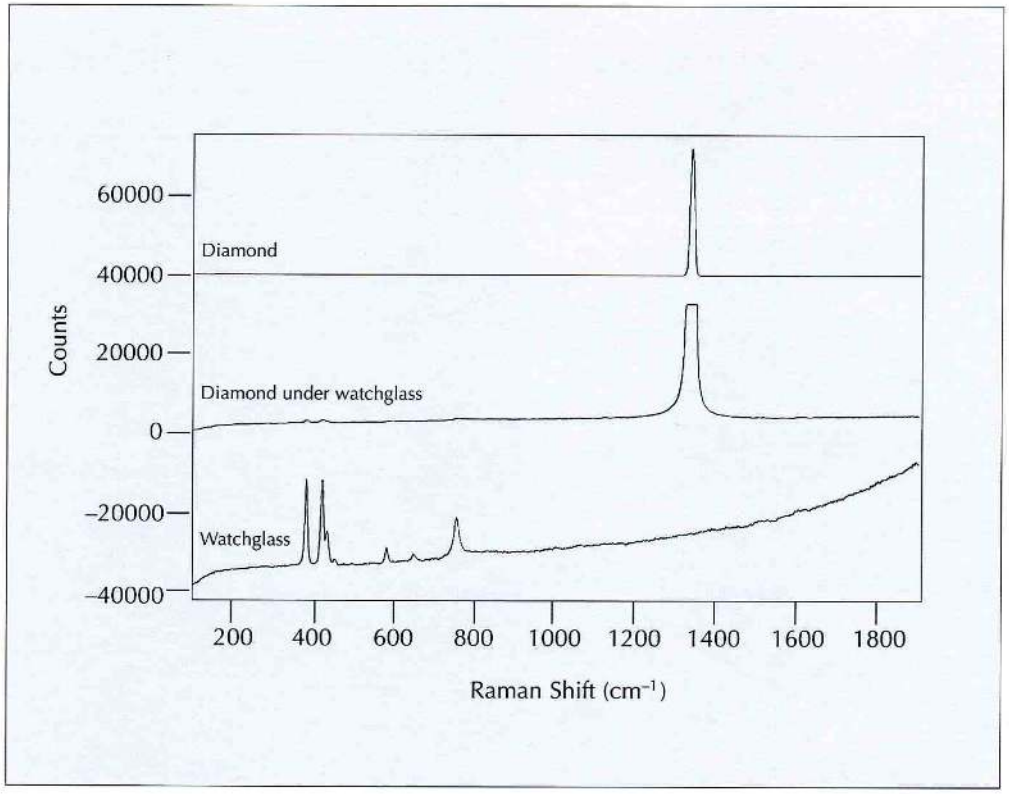


Figure 5b: *Raman spectrum of a diamond under a sapphire watch glass with the comparison spectra of pure diamond and the watch glass.*

and stone can be made. It would seem difficult if not impossible, however, to identify the nature of stones which look like diamond if they are set in a clock face under the watch-glass *(Figure 5a)*. 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 diamond. The sample diagram in *Figure 5b* shows the Raman characteristics of diamond with corundum (as 'glass cover').

A mixed lot of Burmese cut gemstones (kindly donated by Professor Dr E. Gübelin) was mounted table-up with Blu-Tack on a slide *(Figure 6a)*. The Raman spectra were subsequently recorded and the results compared with reference spectra at first selected as the most likely match. Where this did not lead to a satisfactory match of spectral pattern, i.e. identification, the 'strongest peak' table of our search file was taken as a reference. This way the stones could be identified within a very short time. *Figure 6b* shows spectra of seven identified gemstones. Identification by Raman spectroscopy can also be recommended for rough stones, especially when no characteristic visible absorption spectrum can be obtained or expected.

Identification of mounted gemstones set in jewellery may turn out to be difficult when the setting prevents direct contact of a stone with the refractometer. Pieces of jewellery with historical value, e.g. from museum collections, are in many cases adorned with gemstones. However, it is rather rare that such items have undergone gemmological investigations, mainly because until recently hardness testing was still a recognized gemmological technique

Figure 6a: *Seven Burmese stones fixed with Blu-tack on a glass slide and ready for the microscope sample stage. They are from left to right: peridot, diopside, spinel, amethyst, tourmaline, scapolite and datolite.*

Figure 6b: *Raman spectra of the seven Burmese gemstones.*

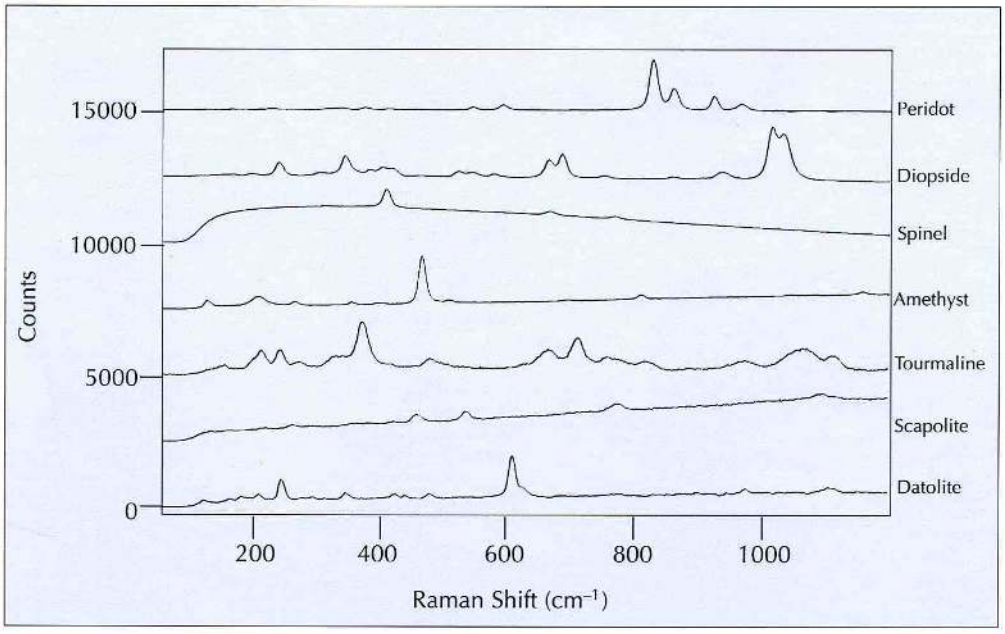


Figure 7: *A bar brooch with a red garnet being analysed on the microscope sample stage.*

Figure 8a: *A dark violet jade cabochon revealed its complex nature under the Olympus BH microscope used in reflected light mode. The darker mineral groundmass was found to be albite feldspar, the lighter crystals are jadeite, magnification 50x.*

Figure 8b: *Raman spectra of jadeite and albite reference material compared with spectra obtained from the two phases in the violet cabochon.*

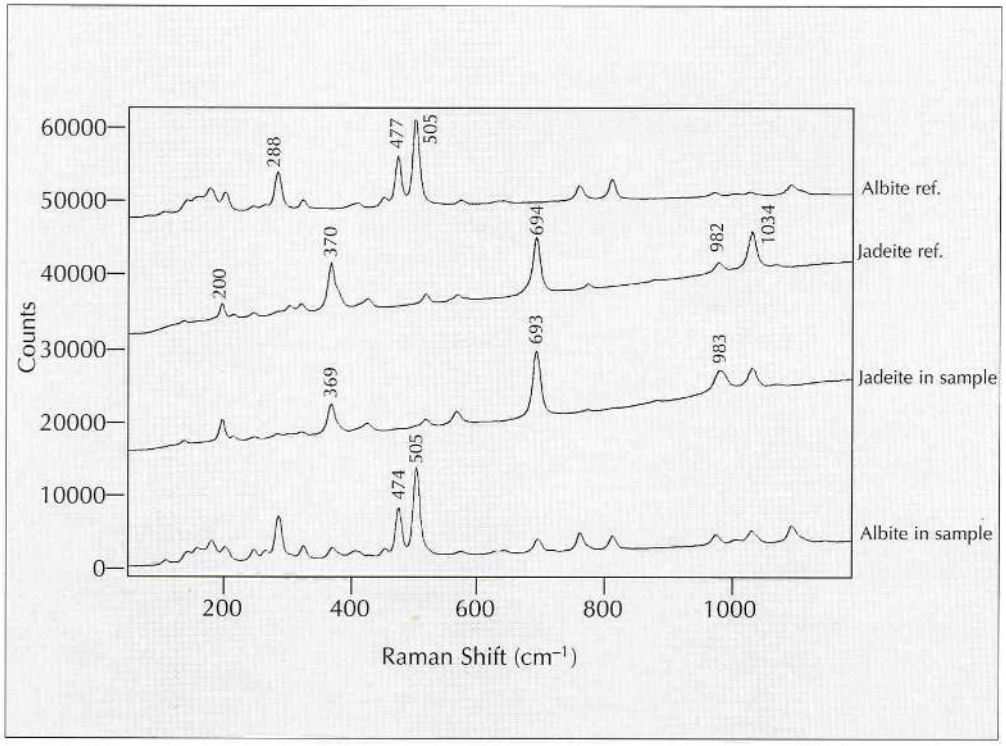


Figure 9: *This prehistoric small axe head (46 mm in length) gave Raman lines of tremolite-actinolite.*

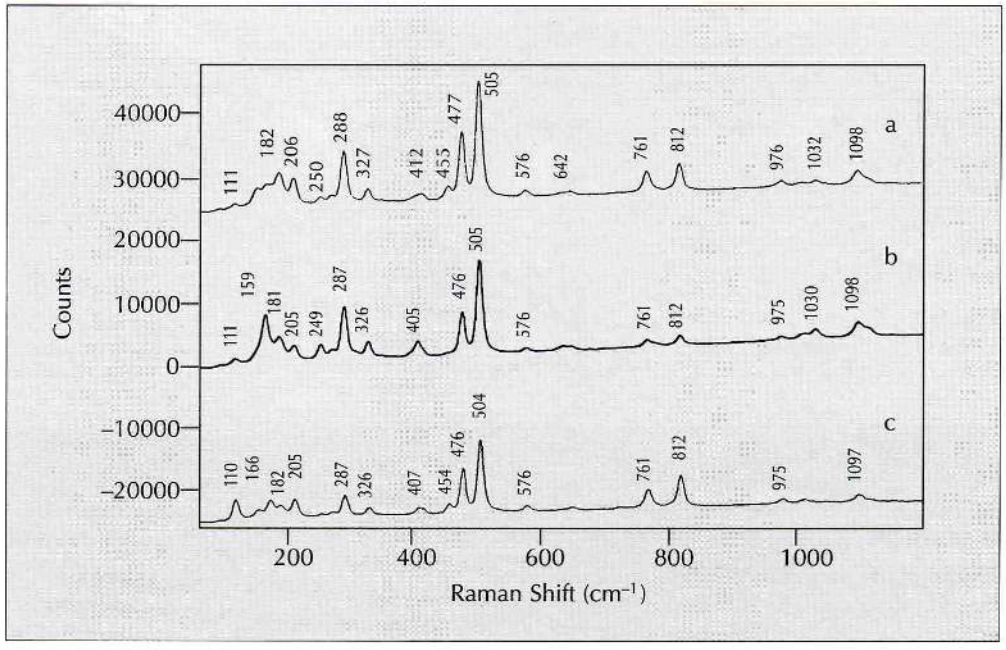
by too many 'identifiers'. Raman spectroscopy now offers an entirely non-destructive means of identification which does not even require mechanical contact between the gem and the analytical tool. This opportunity will hopefully lead to more investigations of museum jewellery (Superchi, 1995).

The brooch shown in *Figure 7* contains a red stone which was easily identified as a garnet from its Raman spectrum, and the optical absorption spectrum confirmed the result.

A violet cabochon was purchased in Mae Sot (Thailand), a market-place for Burmese gemstones. The dark violet colour and the strange structure observed under the microscope first indicated an opaque artificial glass, but a reflected-light image indicated two phases in the material *(Figure 8a)*. Needle-like crystals were recognized and quickly identified as jadeite in a groundmass of lower lustre which was found to be plagioclase feldspar. The closest match in our data base of Raman spectra was found to be that of albite. The spectra of the two components of the gemstone are presented in *Figure 8b* together with the two related reference spectra of jadeite and albite.

Bustamite, a rare gem material, is difficult to identify safely with traditional gemmological means, especially when it has a composite polycrystalline nature and is cut as a cabochon. The values of SG (3.43) and RI (1.67 spot reading) are not conclusive. For the identification of this piece we were also considering the possibility of

Figure 10: *Three Raman spectra of an albite crystal, taken in three directions perpendicular to each other. The directional recording of spectra shows anisotropy with respect to the peak heights, but not the peak positions.*



friedelite, another manganese silicate mineral. The Raman spectrum, however, when compared to a bustamite reference (collection of NMBS) allows instant identification. The bustamite reference file, with its major peaks, is shown in line 101 of *Table I.*

A prehistoric axe head (Figure 9) fashioned from an unknown fibrous whitish material was tested for the Laboratory of Prehistoric History of Basel University. Also, for archaeological material, a non-destructive identification technique is a requirement. The spectrum obtained was immediately recognized as a mineral of the amphibole group, the closest fit being with tremolite. In gemmological circles, massive tremolite-actinolite rock is often referred to as nephrite, and is a well known material used to make Stone Age tools. Nephrites are usually greenish due to their iron content (or portion of actinolite in solid solution), but the present sample has a composition close to the iron-free end of the series, i.e. tremolite.

Limitations

Although the cited literature and examples described above prove the importance and usefulness of Raman spectroscopy to gemmology and associated sciences, the method also has some limitations.

The only major subset of materials that do not yield usable Raman spectra are substances such as metals and alloys, characterized by a simple composition and a high symmetry.

Anisotropic minerals produce Raman spectra which can be very different depending on the relative orientation of the laser and the crystal lattice. Fortunately the wave-number position of the peaks is the same in the spectra obtained from every direction. It is only the relative intensity which may vary with the direction. Therefore, when using a data base for spectral comparison which is based on wavelengths of the strongest peaks, one must bear in mind that the sequence from strongest to weakest may change with orientation. An example of small directional differences among Raman spectra in the x-, y- and z-directions of an albite crystal is shown in *Figure 10.* Other minerals, such as phyllosilicates, may show significantly stronger directional differences in their spectra.

We have already remarked upon the general difficulties in getting useful Raman spectra from dense mineral aggregates such as turquoise, howlite, mother-of-pearl, etc. The spectra of such materials suffer from a high contribution of fluorescence radiation, although in some situations the fluorescence can be reduced by reducing the laser power and increasing the measuring time. This could result in a better peak/background ratio.

Although Raman microprobe investigations of gems are generally non-destructive, accidents may still happen with a small number of thermally unstable minerals (e.g. pyrargyrite, hydrated arsenates) or with some organic materials, so care should be exercised in deciding laser intensity and measuring time.

Fluorescent minerals such as ruby and spinel may produce a high amount of non-characteristic fluorescence radiation which might inhibit the analysis of an inclusion. Again, the reduction of the excitation and/or increase of scanning time may help to overcome the problem. In some situations where, for example, organic fillers in emeralds have to be identified, it is also possible to record peaks for an identification in spectral areas where the general fluorescence is small. Luminescence spectra may themselves provide analytical information where the Raman lines are swamped by fluorescence.

When equipped with a standard Olympus microscope the sample stage of the Renishaw Raman Microprobe can be lowered through approximately 15 cm. This free space between the objective and the sample's lower end is a limitation, although it will accommodate most gemstones. For larger pieces, such as a carving or a vase, the fitting of a special microscope objective which reflects the beam through 90° to the side of the microscope, often enables successful collection of data.

Conclusions

Raman spectroscopy offers a wide field of application in which mineralogical and

gemmological identifications play a major role. The fact that this spectral technique is usually non-destructive, is of inestimable value not only in gemmology but also in related sciences such as archaeology. Not only the host mineral but also inclusions can frequently be identified. An important application in gemmology for Raman spectroscopy is the detection of the nature of organic fracture fillings in emeralds. Raman spectroscopy can also aid the identification of gemstones set in jewellery when the usual gemmological identification methods such as determination of the density and refractive index or visible spectroscopy cannot be applied.

Acknowledgements

We are grateful to the following institutions and persons for providing reference material to start creating our reference data base: the mineralogical section of the Museum of Natural History in Basel, Switzerland (Professor S. Graeser and Dr J. Arnoth), G. and E. Keller (Bettingen, Switzerland), Mr M. Schuler, Mineralogical Institute of Basel University. We wish to extend our thanks to Professor D.C. Smith for reviewing the original paper, and for his valuable suggestions.

References

Bruder, B., 1995. Charakterisierung von Rubinen und Saphiren mithilfe von Flüssigkeitseinschlüssen. Diplomarbeit, Min.-Petr. Institut der Albert-Ludwigs Universität Freiburg

Delé-Dubois, M.-L., Dhamelincourt, P., and Schubnel, H.-J., 1980. Etude par spectrométrie Raman d'inclusions dans les diamants, saphirs et émeraudes. *Revue de Gemmologie, a.f.g.*, **63**, 11–14 and **64**, 13–14

Delé-Dubois, M.-L., Merlin, J.C., and Poirot, J.-P., 1981. Pigment's determination of the calcareous exoskeleton of corals by means of Raman spectra. *Hoseki Gakkaishi*, **8**(1–4), 161–8

Delé-Dubois, M.L., and Merlin, J.C., 1986. Etude par spectrométrie Raman de la pigmentation du squelette calcaire du corail. *Revue de Gemmologie a.f.g.*, **68**, 10–13

Dhamelincourt, P., and Schubnel, H.-J., 1977. La microsonde moléculaire à laser et son application dans la minéralogie et la gemmologie. *Revue de Gemmologie*, **52**, 11–14

Dubessy, J., Poty, B., and Ramboz, C., 1989. Advances in C–O–H–N–S fluid geochemistry of fluid inclusions. *Eur. J. Mineral.*, **1**, 517–34

Griffith, W.P., 1987. Advances in the Raman and infrared spectroscopy of minerals. Chapter 2 in: Clark, R.J.H., and Hester, R.E. (Eds.): *Spectroscopy of Inorganic-based Materials*. Wiley & Sons, 119–86

Hänni, H.A., 1992. Identification of fissure-treated gemstones. *J. Gemm.*, **23**(4), 201–5

Hänni, H.A., 1993. Spectroscopy and its application in gemmology. *J. Gemm. Assoc. HK*, **16**, 16–22

Kiefert, L., Schmetzer, K., Krzemnicki, M.S., Bernhardt, H.-J., and Hänni, H.A., 1996. Sapphires from Andranondambo area, Southern Madagascar. *J. Gemm.*, **25**, 185–209

Koivula, J.I. 1980. Carbon dioxide as a fluid inclusion. *Gems & Gemology*, XVI(12), 389–90

Lasnier, B., 1995. Utilisation de la spectrométrie Raman en Gemmologie. *La Gemmologie dans 'Analysis Magazine'*, **23**(1), 16–18

Maestrati, R., 1989. Contribution à l'édification du catalogue Raman des gemmes. Diplôme d'Université de Gemmologie, Université de Nantes

Malézieux, J.-M., 1990. Contribution of Raman microspectrometry to the study of minerals. Chap. 2 in: Mottana A., and Barragato, F. (eds.), *Absorption spectrometry in mineralogy*, Elsevier Science Publishers, Amsterdam

McMillan, P.F., 1989. Raman spectroscopy in mineralogy and geochemistry. *Ann. Rev. Earth Planet Sci.*, **17**, 255–83

McMillan, P.F., and Hofmeister, A.F., 1988. Infrared and Raman Spectroscopy. Chap. 4 in: Hawthorne, F.C. (Ed.), *Spectroscopic methods in mineralogy and geology*, Mineral. Soc. America Reviews, **18**, 99–159

Peretti, A., Mullis, J., and Kündig, R., 1990. Die Kaschmir-Saphire und ihr geologisches Erinnerungsvermögen. *Forschung und Technik in 'Neue Zürcher Zeitung'*, 15 August, 59

Pinet, M., Smith, D., and Lasnier, B., 1992. Utilité de la microsonde Raman pour l'identification non destructive des gemmes. In La Microsonde Raman en Gemmologie, *Revue de Gemmologie a.f.g.*, No. hors série, 11–61

Schmetzer, K., and Medenbach, O., 1988. Examination of three-phase inclusions in colorless, yellow and blue sapphires from Sri Lanka. *Gems & Gemology*, **24**, 107–11

Schubnel, H.-J., 1992. Une méthode moderne d'identification et d'authentification des gemmes. In La Microsonde Raman en Gemmologie, *Revue de Gemmologie a.f.g.*, No. hors série, 5–10

Smith, D.C., 1987. The Raman spectroscopy of natural and synthetic minerals: A review. Georaman-86. *Terra Cognita*, **7**, 20–1

Stern, W.B., and Hänni, H.A., 1982. Energy-dispersive X-ray spectrometry: a non-destructive tool in gemmology. *J.Gemm.*, **18**, 285–96

Superchi, M., 1995. Interesting Raman results at CISGEM. *ICA Gazette*, December 1995, 5–6

Themelis, T., 1990. Oiling emeralds. *Cornerstone*, July, 21–4

Williams, K.P.J., Pitt, G.D., Batchelder, D.N., and Kip, B.J., 1994. Confocal Raman microspectroscopy using a stigmatic spectrograph and CCD detector. *Applied Spectroscopy*, **48**, 232–5