

# Identification of filler substances in emeralds by infrared and Raman spectroscopy

Dr L. Kiefert<sup>1</sup>, Professor H.A. Hänni<sup>1</sup>, J-P. Chalain<sup>1</sup> and W. Weber<sup>2</sup>

1. SSEF Swiss Gemmological Institute, Falknerstrasse 9, CH-4001 Basel, Switzerland

2. Rainstrasse 4, CH-8330 Pfäffikon, Switzerland

**ABSTRACT:** For many centuries, fissures in emeralds have been filled with oils and other natural substances to enhance their clarity. For approximately 15 years, the substances used also comprise various artificial resins, mainly epoxy resins. The various substances have different stability, but none of the treatments is permanent. Oils are the most volatile of the fissure filling media used, but the stone can easily be cleaned and refilled. Artificial resins, on the other hand, are much more durable, but they also decompose with time and are then hard to remove. Because of this, some traders require an identification of these substances which can be performed by infrared and/or Raman spectroscopy.

The first step in fissure filler identification is visual observation by the microscope and under long-wave UV-light to estimate the presence or absence of a filler and its position in the stone. Then the filler is identified with one or both of the above-mentioned methods. At the SSEF laboratory, which pioneered the techniques in a complementary way, infrared spectroscopy is used as a macro method and Raman spectroscopy as a micro method. Once a spectrum is obtained with either method, it is compared to the extensive data bank of either infrared or Raman spectra of the pure filler substances. The present paper summarizes common emerald fillers and describes in detail their identification with infrared and Raman spectroscopy.

**Keywords:** emerald, fissure fillers, infrared, oil, Raman, resin, spectroscopy

## Introduction

Most varieties of beryl (aquamarine, yellow beryl, morganite) are generally quite clear and do not contain important inclusions. The clarity of emerald, in contrast, is usually affected by the presence of healed or open fissures. While aquamarines have grown with little

interference in pegmatite dykes and pneumatolytic druses, most emeralds were formed in metamorphic rocks and underwent a more agitated geological history. Shearing forces and fluid action due to metamorphic processes led to mineral transitions and any rigid and large gem mineral crystals were prone to crack or break under the pressure with consequent

Table 1: Selection of filters analysed at SSEF.

Category	Trade name
oil	Universal Oil (paraffin oil); Johnson's Baby oil; 'MAZOLA' pure corn oil; olive oil; Clove oil nat 80–82%; Roth AG; cedar wood oil, Merck; 17196 H.E. Daniel, chinese cedar wood oil; MC153263 H.E. Daniel, 100% nat. cedar wood oil; CE108 Spectrum Quality Products cedar wood oil; 21695 H.E. Daniel 100% nat. Virginian cedar wood oil; 23292 H.E. Daniel 100% nat. cedar wood oil; Merck Cedarwood oil for microscopy; Panreac purified cedar oil; Cedro oil, Colombia; BPC FIG 34 cedarwood oil thick micro
coloured oil	green Joban oil, India
oil/wax	paraffin wax; wax from F.Hakimian, N.Y.; sperm whale oil (hardened)
Canada balsam	hardened; for microscopy; 100% natural, ref M; synthetic, ref Go
artificial resin	Opticon (epoxy resin); Palm oil, Palma (epoxy resin); Permasafe (bisphenole A); 77–309.RM (bisphenole A); Caldofix Struers; Epoxy 330; Scandiplex A 911E; LV 15 (UV-hardening resin)
silicon	'Silicon DC4' silicon fat; Luster's PCJ Nutrientsheen 3 silicon oil

formation of fissures. Should physical and chemical conditions still be favourable to crystal growth after the main destructive event, healing of damaged crystals may take place together with continued growth. If breakage and fissure formation in the gem crystals occurred at a much later period, e.g. during the blasting of the parent rock, the defects stay unhealed and artificial fissure treatment then becomes a commercially attractive step for the miner or stone dealer.

The clarity of an emerald is reduced by the presence of inclusions – guest crystals, internal cavities or negative crystals, healing fissures, structural features and by open fissures. The latter are especially visible in Colombian emeralds because most are otherwise relatively inclusion-free. In emeralds from other countries (e.g. Brazil, Russia, Zambia, Zimbabwe-Sandawana, Afghanistan and India) crystalline inclusions are more frequent, but fissures are still present (see e.g. Gübelin and Koivula, 1986; Epstein, 1989; Kazmi and Snee, 1989; Laskovenko and Zhernakov, 1995; Zimmermann *et al.*, 1997).

To improve the clarity of emerald open fissures may be disguised by impregnating the stones with some more or less permanent colourless substances. Although coloured oils and resins are also used to fill emeralds,

we do not focus on these substances in this publication. Effective fillers have refractive properties close to those of emerald. Such substances comprise oils (natural or synthetic), resins (natural or with a natural resin base), glues or artificial resins (Table 1). Fissure treatments have been carried out for years – see Ringsrud (1983), Nassau (1984), Hänni (1988), Hurwit, (1989), Themelis (1990), Kane (1990), Kammerling *et al.* (1991), Bosshart (1991a), Shida (1991) and Koivula *et al.* (1994).

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. When the treatment was performed on rough stones it masked the real appearance of the emerald and inhibited reliable estimation of their true quality. Furthermore, the durability of the new substances was questioned when decomposition of the originally 'invisible' filler was reported in some stones by Kammerling *et al.* (1991) and Federman (1998). The fillers had turned white and totally spoiled the stone it was originally supposed to have improved. Therefore an increasing number of people involved with emeralds wanted to identify epoxy-treated stones, knowing from articles in the gemmological literature that such an

identification is possible (e.g. Hänni, 1992; Kammerling *et al.*, 1995; Kiefert and Hänni, 1996; Chalain *et al.*, 1998; Johnson *et al.*, 1998).

The present paper is an attempt to guide laboratories in identification of fissure fillings in emerald, if required. Appropriate optical and spectroscopic properties of emerald filler substances are described. Based on gemmological needs and the results of early analyses of one of the authors (WW), the substances are divided into three major groups, namely oil, Canada balsam, and artificial resin (see *Table 1*). Under these headings, methods for the detection and identification of enhancements in emeralds are described in detail. The following two steps are necessary to obtain reliable results: observation by optical means and identification with analytical instruments.

### Fissure treatments

Open fissures of emeralds are filled with substances (air, for example) with a refractive index significantly different from that of emerald. Light entering the emerald, even at high angles of incidence to the fracture, is reflected off the surface of the fracture and it behaves as if it were a mirror. When these fractures are filled with substances with a refractive index close to that of the emerald the light can pass through the fractures with almost no reflection. This cancels out the mirror effect and the visibility of the fracture is greatly reduced.

In Colombia, Brazil, and the majority of the other emerald producing countries, treatments of emerald fissures are first carried out on the rough material. If cutting intersects unfilled fissures, further treatment may take place. Fissure fillers usually are heated to reduce their viscosity. The substances are then introduced into emerald fissures using various vacuum or pressure techniques (*Figure 1*). A number of emerald dealers call this technique 'oiling' (Ringsrud, 1983) regardless of the kind of substance used. This causes confusion among inexperienced buyers who think the treatment of emeralds is performed with oil only.



*Figure 1: Vacuum chamber on heating stage. This system is in use at the Institute of Earth Sciences of Basel University for hardening porous rocks to make them workable. For emerald treatment, the cleaned stones are evacuated above the filler, and then lowered into the substance. Normal pressure is admitted when the liquid has penetrated into all open fissures and fractures. © SSEF Swiss Gemmological Institute.*

In the past, the fact that treatments of gemstones have not been communicated or declared has caused considerable damage to the confidence of consumers. Sales figures appear to have gone down directly due to law cases concerning filled emeralds which were reported by the media. Nowadays most trade associations expect dealers to disclose the product that has been used for enhancement. But such disclosures are not always made, and with many older stones it is not clear to the owner whether such stones have been

treated. The situation is further complicated by possible multiple treatment with different substances at different trade levels.

The various colourless oils, either natural or synthetic, appear to be well accepted among the trade. Artificial resins, however, which have been used for emerald treatment for about 15 years, are accepted by fewer in the trade. The reasons for this difference in acceptance may be the following.

Oils are mobile to viscous, simple to introduce into fissures, but also prone to escape if in contact with liquid detergent. The fissures are comparatively easy to clean out, and stones are readily re-oiled. The improvement in appearance due to oil is less than with resins since the refractive indices of oils are lower (Chalain *et al.*, 1998). To many jewellers the fact that a customer may recognize the real state of an emerald when the oil drains or dries out may lead him to favour resinous substances.

Artificial resins are more viscous and may possess a solidifying character, which the oils do not have. Fresh artificial resins with higher refractive indices give a better enhancement to a stone. They adhere well in the fissures, but are difficult to dissolve and replace should they have changed their appearance or decomposed.

It is also worth noting that the stability of the treatments with organic substances is difficult to define and depends on the time and temperature specified. When an announcement appears in the trade press that a well known filling product should at the same time be 'permanent' and also 'removable' it casts doubt on its stability. Compared to the durability of an emerald, which can be worn for many centuries without damage, none of the treatments should be considered as stable.

Green fillers are also applied to enhance not only the clarity but also the colour of emerald using green Joban oil, green Opticon etc. This treatment, mainly practised in India, is easily visible under magnification. Emeralds treated in this way must be called 'treated emeralds' according

to CIBJO rules (CIBJO, 1991, 1997). This type of treatment is, however, not considered in this article.

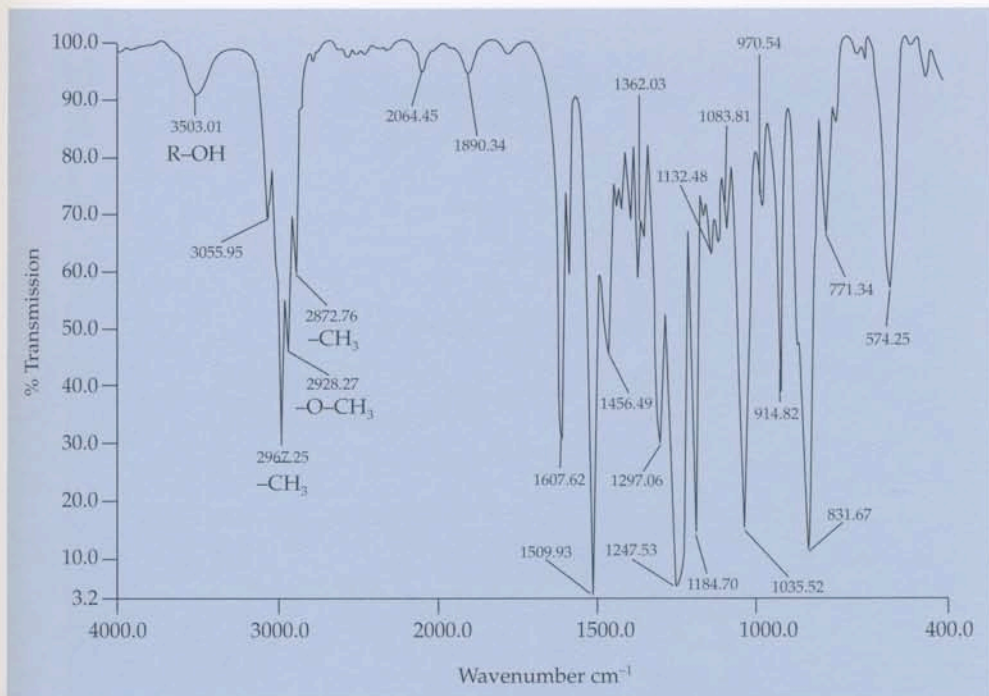
Colourless substances in emerald fractures are more difficult to detect than coloured substances. Some substances have a refractive index so close to that of the emerald that when observed with the unaided eye, the fracture disappears almost completely.

### Spectroscopic properties of pure filler substances

The organic substances used to fill emeralds either alone or mixed, are commercially available. Therefore, their properties are well known and Fourier transform infrared (FTIR) and Raman spectra are readily available (e.g. Hummel, 1990).

All available organic substances at the SSEF Swiss Gemmological Institute which could be used to fill emerald have had their infrared spectra recorded and the major characteristic peaks related to the chemical bonds (Figure 2, see Hummel, 1990). Since 1991, 42 possible filler substances have been characterized at SSEF with FTIR spectroscopy and stored in a reference library for comparison. These include various oils and waxes, among them various natural and synthetic cedarwood oils and Canada balsams, clove oil, olive oil and paraffin oil as well as various epoxy resins such as Opticon, Palma (Palm Oil) and Permasafe which was available in a polymerised state. Initially, use of the term 'Palm Oil' was confusing for those in the trade, until the substance proved to be an epoxy resin made by Shell and marketed under the name 'Epon 828'. The analysed products were supplied by a number of customers, emerald treaters and chemical companies. The technical or trade names of a selection of these substances are listed in Table 1.

The Raman spectra of the most important filler substances have also been recorded since 1995 at SSEF and stored in a reference library. The spectral area lying between 1200 and



**Figure 2:** Infrared spectrum of Epon 828, showing the chemical bonds related to the various peaks. © SSEF Swiss Gemmological Institute.

3200  $\text{cm}^{-1}$  contains the characteristic Raman peaks for the kind of organic substances used for fissure fillers without interference from the Raman peaks of emerald (see below).

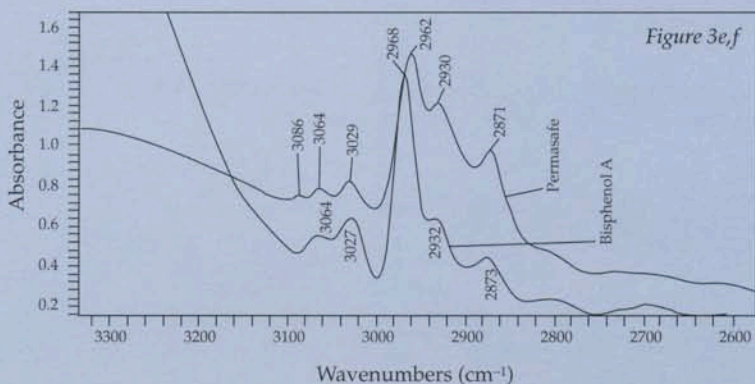
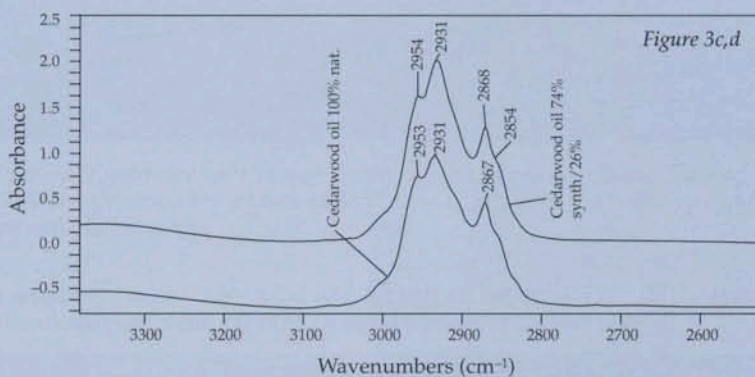
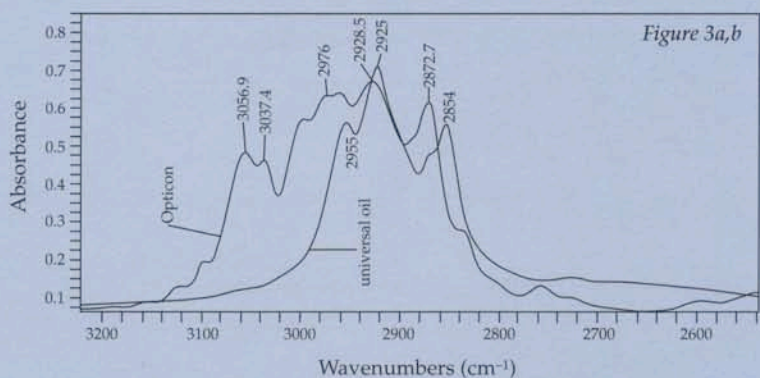
According to their spectroscopic properties, which are closely related to their physical properties, the fillers can be divided into three groups: oils, Canada balsam, and artificial resins (see *Table I*). While we could not establish any reliable difference between the spectra of natural and synthetic oils or Canada balsams, distinct differences were observed between the spectra of oils or Canada balsams on the one hand and artificial resins on the other (see below).

#### FTIR spectra of pure substances

After having verified the identity of the substances in the characteristic spectrum region below 2000  $\text{cm}^{-1}$ , we concentrated on the peaks in the 2800–3100  $\text{cm}^{-1}$  range which do not suffer interference from emerald absorption.

A comparison of FTIR spectra of oils and artificial resins shows that the general distributions of their absorption peaks are very similar between 2800 and 3000  $\text{cm}^{-1}$ . This is not surprising since the peaks in this part of the spectrum are due to C–H vibration bonds which are present in both organic substances. An experienced spectroscopist may, however, note that the relative absorption heights of the peaks at 2870 and 2854  $\text{cm}^{-1}$  may differ in oils and artificial resins (*Figure 3a,b*). This difference can be interpreted as giving an indication of one or the other substance, but should not be considered as strictly characteristic, as can be seen in the spectrum of cedar wood oil (*Figure 3c,d*).

In contrast, it appears that none of the analysed oils (natural or synthetic) show significant absorption above 3000  $\text{cm}^{-1}$ , while all artificial resins show clear and typical absorption (*Figure 3a–d*). Therefore, the peaks between 3000 and 3100  $\text{cm}^{-1}$  are important in distinguishing oils from



**Figure 3:** FTIR spectra of: (a) universal oil; (b) artificial resin (Opticon) showing that the absorption features of the 2854 and 2870 peaks are different in intensity and that absorption features are very different in the 3000–3050  $\text{cm}^{-1}$  area; (c) and (d) cedarwood oil; (e) Permasafe; (f) bisphenol A. © SSEF Swiss Gemmological Institute.

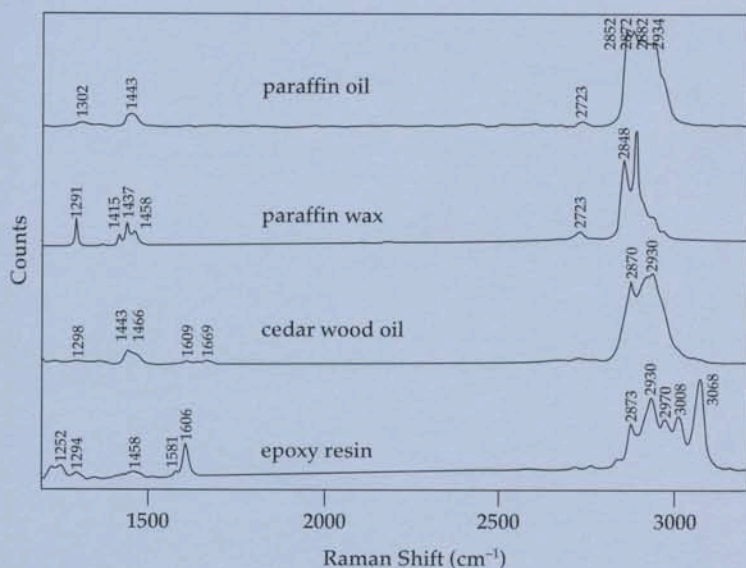
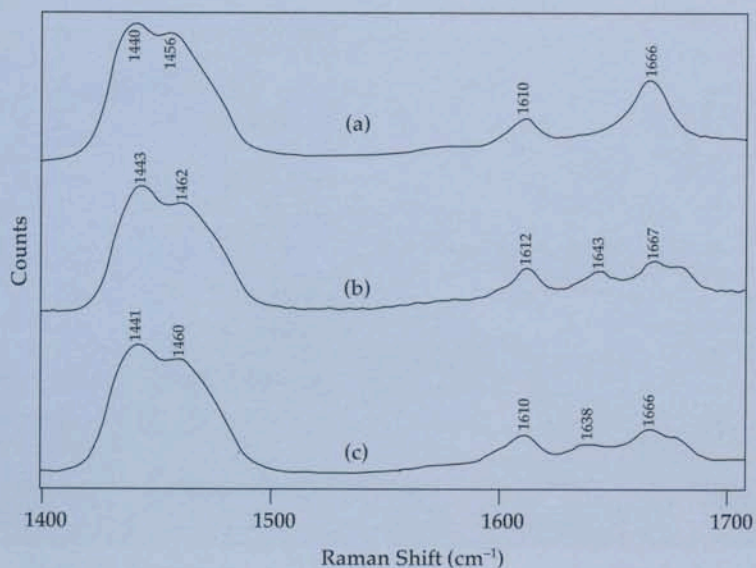


Figure 4: Part of the SSEF reference collection of Raman spectra of emerald fillers. The four spectra contain peaks at different wavenumbers and an identification of products is possible by comparison. © SSEF Swiss Gemmological Institute.

Figure 5: Raman spectra of various cedar wood oils: (a) natural cedar wood oil; (b) synthetic cedar wood oil; (c) 74% synthetic cedar wood oil. © SSEF Swiss Gemmological Institute.



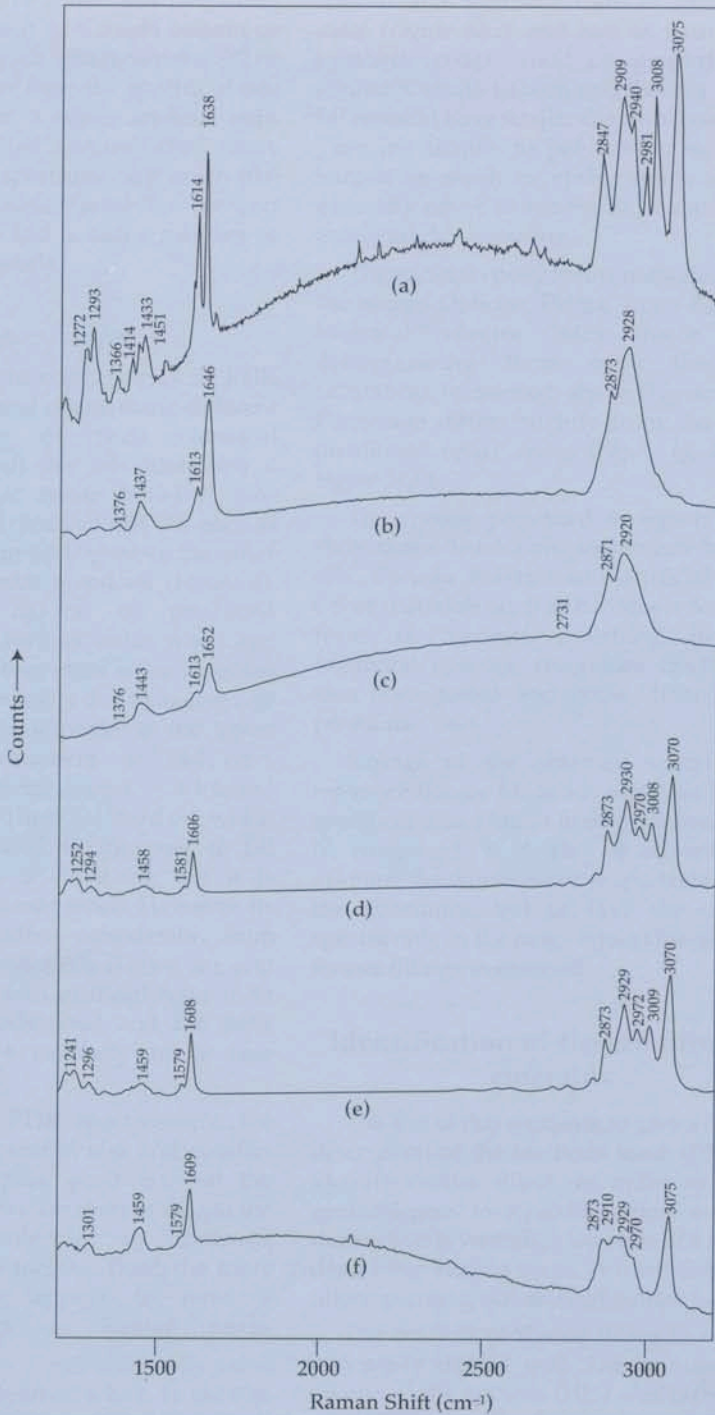


Figure 6: Raman spectra of (a) clove oil; (b) natural Canada balsam; (c) synthetic Canada balsam; (d) Opticon; (e) Palm oil; (f) Permasafe. (d), (e) and (f) are epoxy resins. © SSEF Swiss Gemmological Institute.



artificial resins. Some other, less frequently used substances such as Canada balsam or clove oil have other characteristic FTIR spectra which differ from the spectra of oils and artificial resins. A newer artificial resin which is marketed under the name 'Permasafe' has a spectrum very much like the other epoxy resins (Figure 3e,f, see also Fritsch *et al.*, 1999) and is also a member of the Bisphenole A family.

#### *Raman spectra of pure substances*

In Raman spectroscopy, just as in FTIR spectroscopy, oils and resins show different peaks depending on their chemical composition. Of all the oils identified a distinction can be made between two different types: one type includes oils such as mineral and paraffin oil (Figure 4); the other type consists of cedar wood oil (Figure 4), which can be natural or produced synthetically. The various cedar wood oils tested in the laboratory show some variation in peak intensity probably due to ageing and oxidation. Their major peaks in the lower region of wavenumbers at  $1441\text{ cm}^{-1}$ ,  $1445\text{ cm}^{-1}$  and  $1666\text{ cm}^{-1}$  occur in all tested samples (Figure 5). There is a third oil, which may have been used in the past to fill emerald and that is clove oil, but it is identifiable by its strong smell. However, its Raman spectrum differs considerably from the spectra of the other oils (Figure 6a), and may be confused with artificial resin if its smell has been undetected and the peak measurements not carefully made (see Figure 6d,e,f).

In contrast to FTIR spectroscopy, the Raman spectra of paraffin wax and paraffin oil show similar peak positions, but the peaks of paraffin wax are sharper due to the fact that the molecules in hardened substances are less mobile. Thus, the more liquid substances appear to have a broadening effect on Raman peaks (Figure 6a).

One organic substance which is used to fill emerald fissures is Canada balsam which may occur as a natural resin but may also be produced synthetically. The properties of

natural and synthetic Canada balsam are alike (Figure 6b,c) and just as natural and synthetic cedar wood oil properties are similar, Canada balsam and the oils used to fill emerald have similar chemical properties. They are unable to polymerise, so do not harden as much as epoxy resins and are generally easier to remove from the stone if they start decomposing.

The various epoxy resins marketed under the names Opticon, Palma, Epon 828, have identical spectra with major peaks distinguishing them from the other substances mentioned above (Figure 6d,e,f). Permasafe differs slightly from the above-mentioned epoxy resins (Figure 6f, see also Figure 3e,f).

The spectra presented in Figures 4 to 6 show that a distinction can be made between oils, Canada balsam, and artificial resins. Other materials such as hardeners for epoxy resin or various polishing materials (diamond powder, chromium oxide) have also been tested and show distinct peak positions.

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 examine the whole possible spectral range of the substance, but to save the detailed spectra only in the range critical for detecting fissure fillings in emerald.

### **Identification of fissure fillers in emeralds**

The aim of this section is to give a detailed description of the methods used at SSEF to identify fissure fillers. In order to enable gemmologists to reproduce these methods, this section is written in the style of a manual describing various steps in identification of fillers, pointing out any difficulties.

The analysis of fissure filling in emerald previously treated with known substances by one of the authors (HH) was carried out with FTIR as well as Raman spectroscopy on several stones and proved that the methods produced spectra comparable with the pure

## Instrumentation

For successful identification of fissure fillers in emeralds, thorough analysis with a gemmological microscope, observation under UV light, and identification with FTIR and/or Raman spectroscopy are essential.

At the SSEF laboratory, microscopic observation is performed with a gemmological microscope by Bausch & Lomb, allowing magnification up to 70x. The UV source used is a long-wave (365 nm) UV lamp which is part of the Dialite lamp supplied by System Eickhorst.

The Fourier Transform infrared spectrometer used at the SSEF is a Philips PU9800 instrument with Nicolet software OMNIC. An additional software package from Nicolet which contains a number of IR data collections including Hummel (Polymer), Organics by Raman, Sigma Biological Sample Library, Crime Lab Sample Library, and Aldrich Sample Library allows the direct comparison of a measured spectrum with stored data and its identification.

A Renishaw 1000 Raman system equipped with a CCD Peltier detector and an argon ion laser (514 nm) with a power of 25 mW was used for filler identification. The objective lenses on the microscope are Olympus BH lenses with x5, x10, x20 and x50 magnification. Raman analysis with this system can be performed in two modes. The first is a mode in which data points are collected over a selected range of wavenumbers for a certain time; the range can be chosen by specifying a centre wavelength, and then the system automatically collects data several hundred wave numbers to each side. The second mode, the extended mode, collects data successively over the pre-chosen area. This type of analysis makes it possible to cover any scan range from 100 to 9000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  (Ostertag, 1996; Hänni *et al.*, 1997). Up to 1999, spectra were collected using Renishaw software, and then translated into the software package GRAMS/386. Since 1999, with the aid of an upgrade of both the Renishaw and the GRAMS software, spectra are directly recorded in GRAMS.

substances. During the last five years, successful identifications have been obtained on more than 500 stones from customers of the laboratory.

### Observation

*Observation of fissures with the microscope;* for the observation of an emerald treatment, a 10x loupe is not always sufficient, while a detailed study with the microscope generally allows the detection of a filler substance in the emerald. It also gives information about the extent of treatment and one may also form an opinion about the nature of the filler. Fractures filled with foreign, artificially-introduced substances commonly appear different from those occupied by natural fluids. Fissures which contain natural fluids (notably aqueous brine) are often oriented

parallel to one of the crystal faces, and commonly consist of more than one phase (liquid, vapour or solid).

Trapped individual gas bubbles or extended 'lakes' of air are a reliable indicator for the presence of an artificial filler. Frequently, dendritic to lobular structures can be observed, showing the distribution between the (liquid) filler and a gas phase; the oils or resins have refractive indices close to that of emerald. As a function of the thickness of the fissure, an effect due to the dispersion of light may be observed which resembles the 'flash effect' observed in fissure filled diamonds (Nelson, 1993).

While oil may create an orange flash effect, flashes which change their colour in different light positions appear to be due only to artificial resins (Figure 7; Kammerling

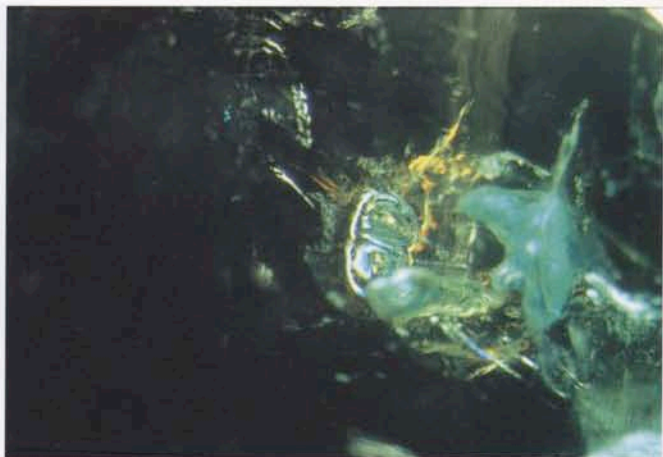
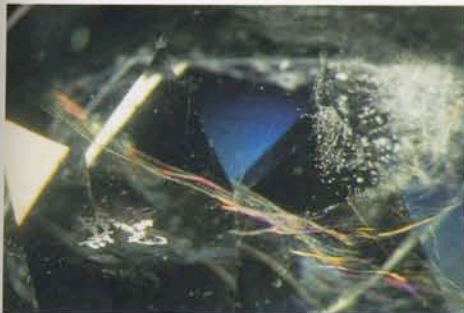
*et al.*, 1995). Depending on the orientation of the fibre optic light, the flashes may be orange, violet, or blue, the blue colour being mainly visible when observed almost along the fissure plane. However, multicolour flashes are not always present in fissures treated with artificial resin, and single colour orange flashes are frequently observed.

When fissures are not filled completely, dendritic patterns and worm-like structures may be observed, sometimes with trapped air bubbles (Figure 8). The nature of these structures gives an indication of the viscosity of the filler but cannot be used for identification.

On drying, the fillers may become opaque and then the treated fissures are readily visible (Figure 9). This is generally the point when identification of the filler becomes a factor of significance for buyers of emeralds.

Before any instrumental analysis is performed, it is important to use the microscope to locate the most easily accessible fillers. The necessary lighting includes reflected light, dark field and/or fibre optic illumination. The latter allows a strong and precise lighting, but, more importantly, easier and more flexible observation in different directions. Holding the emerald with tweezers prevents the surface of the stone becoming greasy from handling and allows light to enter the stone more easily.

**Figure 7:** Colour flashes from an epoxy resin treated fissure in an emerald. The resin has a refractive power close to that of emerald and the colours are due to a dispersion effect. © SSEF Swiss Gemmological Institute.

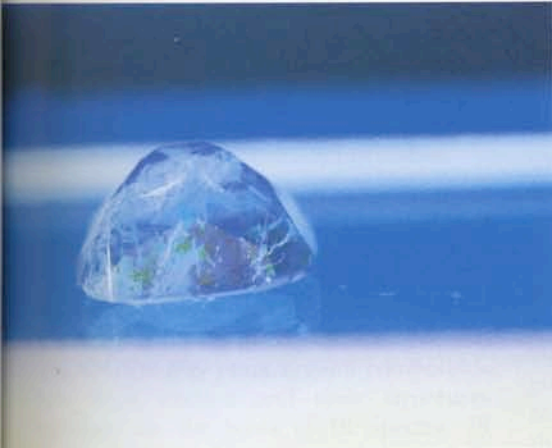


**Figure 8:** Trapped air bubbles and dendritic pattern in an epoxy resin-treated emerald. © SSEF Swiss Gemmological Institute.

*Observation of emerald fissures under UV light:* The use of long-wave UV light (365 nm) is a convenient tool to observe fissure fillings in emeralds. The stone is placed on top of the UV light source and may be inert or show a reddish colour depending on the amount of Cr and Fe in the stone; but a different fluorescence colour may show in the fissures and can indicate the extent of the treatment by virtue of the spread and number of fluorescing fissure planes (Figure 10).

**Figure 9:** Decomposed oil on a fissure plane of an emerald. For various reasons it is possible that filling media dry out or may decompose. Heat, solvents, or ultraviolet radiation may contribute to disintegration and lead to a whitish appearance which may be easily visible. © SSEF Swiss Gemmological Institute.





**Figure 10:** Observation under long wave UV radiation (365 nm) can be an effective method for judging the amount of treatment and for finding the best positions to obtain spectra for filler identification. © SSEF Swiss Gemmological Institute.

Like many organic substances, the majority of substances used to treat fractures in emeralds (oils, balsam, resins) show fluorescence under UV light. In contrast, most natural fluids are inert, although hydrocarbons have been observed and described in Colombian emeralds (Bosshart, 1991b), and it cannot be excluded that they may exhibit a similar fluorescence. Again, artificially filled fissures may not always show fluorescence, especially if the amount is small and the filler fluoresces weakly. Thus, although UV fluorescence may give important information, it should not be considered as a diagnostic test for identification.

Generally speaking, oils show a yellowish fluorescence while many artificial resins that react to UV light show a bluish-white fluorescence. Although not a complete identification tool, this fluorescence allows evaluation of the position and the quantity of filler in the treated fissure (Figure 10). When the fissures are readily visible, it is possible to classify the extent of the treatment. At the International Coloured Stone Association (ICA) meeting in Tucson, 1998, the consensus was to use three categories to classify the

extent: minor, moderate and significant (SSEF Standard and Applications, 1998). It is emphasized that these grades do not replace a judgement by the dealer who has to evaluate the general quality of the stones. For example, if a small single treated fissure is situated at the centre of the table of an emerald, its extent may be classified as minor. But after the substance decomposes, the visibility of the fracture may have a significant impact on the overall appearance of the stone.

The observation of emerald fissures under UV light combined with microscopic observation, allow location of treated fissures in stones and is an important step in preparation for point analysis with the Raman microprobe or with infrared spectroscopy (see below).

Thus observation of emerald fissures with a microscope and UV light enables the gemmologist to conclude if a foreign substance is present or not, and although some features of emerald fillers such as a certain dendritic pattern or a certain UV fluorescence may give an indication of the type of substance present in the emerald, positive identification of the substance can only be carried out by FTIR or Raman spectroscopy.

#### *Identification by spectroscopic analysis*

The identification of individual substances is restricted to laboratory techniques. The first analyses of these substances at SSEF Swiss Gemmological Institute were carried out in 1991 using infrared spectroscopy (see Figure 11), and in 1995 SSEF acquired a Raman spectrometer. Since then both FTIR and Raman spectra have been obtained routinely to analyse fissure fillings in emeralds.

It is important to note that the interpretation of spectra obtained with both techniques relies strongly on comparison with known reference spectra stored in a database. Thorough analyses to characterize the chemical nature of the substances were carried out in 1993 by one of the authors (WW) and led to a decision at SSEF to group the substances into three distinct groups; oil,

Canada balsam, and artificial resin. Any further distinction (such as that between the different types of oils) is too time consuming and difficult to obtain with the spectroscopic means usually present in a gemmological laboratory to be economically justifiable.

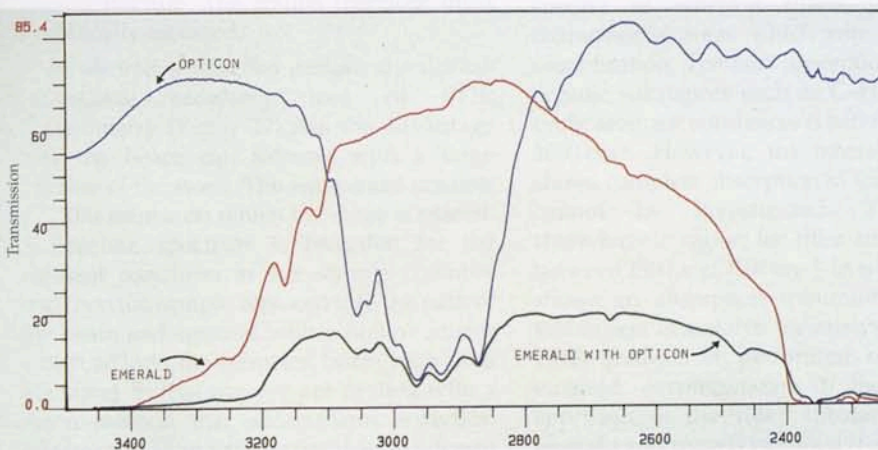
*Methods of FTIR analysis:* Infrared spectroscopy is one of the most efficient analytical techniques to characterize organic materials. IR spectroscopy is a vibrational spectroscopy, which measures the energies of vibrating molecules in the infrared spectral area. For over fifty years, organic compounds have been studied and their structures explained on the basis of IR spectra. IR spectra are considered as characteristic 'fingerprints' for given compounds. Large catalogues and collections of spectra are available to enable identification and comparison when unknown materials are investigated (Hummel, 1990; Moenke, 1962; Sadtler, 1973).

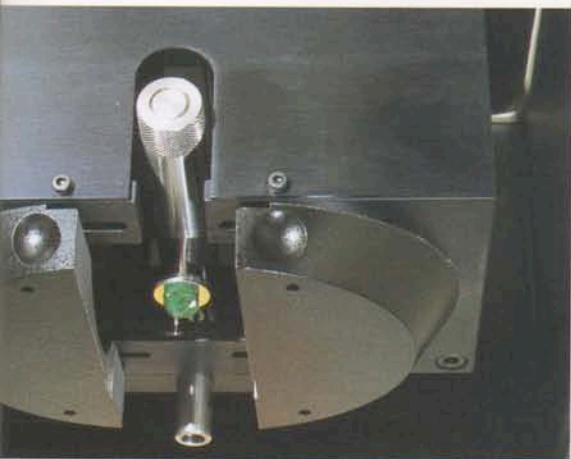
At SSEF, FTIR spectroscopy is performed in two modes: one is direct transmission, where the analysing beam is transmitted through the sample; the other is measurement in reflection-absorption mode using diffuse reflectance equipment where the analysing beam is directed onto the sample placed on a flat mirror and covered

by a hemispherical mirror. Thus the beam is focused through the sample by the mirrors before being collected by the detector. Tests have also been performed in a third mode, with a 5x beam condenser (KBr lens), but the signal obtained with the diffuse reflectance accessory was stronger and the method quicker.

Although the majority of samples are best analysed by the diffuse reflectance method, there are samples in which it is necessary to analyse fissure fillings by *direct transmission*, either because they are too large to fit into the sample chamber for diffuse reflection (more than 40 ct), or because they are mounted in jewellery. To perform analysis by direct transmission, a baseline has to be recorded by measuring the infrared beam in the empty sample chamber. After this, the stone, mounted onto a sample holder, is placed into the beam making sure that it does not contact any masking or plastic. In order to obtain good results with FTIR absorption analysis, either a significant amount of filler substance must be in the stone or the infrared beam must be focused through a fracture which has been located previously (e.g., with UV fluorescence). There are several difficulties using the direct transmission method, the main ones being:

**Figure 11:** FTIR spectra from 1991 of untreated emerald (red), of Opticon epoxy resin (blue), and of an Opticon treated emerald (green). Within the transmission area of emerald between  $3500\text{ cm}^{-1}$  and  $2400\text{ cm}^{-1}$ ; the major absorption of the artificial resin is clearly visible. © SSEF Swiss Gemmological Institute.





**Figure 12:** Diffuse reflectance accessory used at the SSEF fitted to the Philips (PU9800) FTIR spectrometer. In contrast to the micro-method of analysis with Raman spectrometry, this type of FTIR analysis is a macro-method giving an average result. © SSEF Swiss Gemmological Institute.

- intersecting at least one larger fissure to give a sufficiently strong filler signal;
- selecting an orientation of the stone so that the emerging beam reaches the detector;
- obtaining a transmitted beam of sufficient energy.

It can take a long time to adjust a stone to produce a measurable signal, and since the path of the beam through the stone cannot be exactly monitored, it could well pass beside a treated fracture. The results therefore must be critically assessed.

In *absorption-reflection analysis* the diffuse reflectance accessory tool of FTIR spectrometry (Figure 12) has the advantage that the beam can interact with a large volume of the stone. The equipment consists of a flat mirror on which the stone is placed. A baseline spectrum is recorded for the ambient condition in the sample chamber and then the sample is placed into the path of the beam and covered with a hollow mirror which reflects the refracted beam back onto the stone. In this way we are dealing with a macro-method that accumulates analytical information from various fissures in different

parts of the stone. Contrary to the analysis of a directly transmitted beam, it is not crucial to look for a special path through the stone (i.e., the beam does not have to be focused on a fracture as precisely as with the direct beam method). The orientation of the stone is, however, important, because the absorption bands of OH-vibrations are close to the spectral area of analysis and cause structural effects which interfere with absorptions of C-H-vibrations of the substance to be analysed (Figure 13).

Generally, better results are obtained when the beam interacts with a larger sample, but if the sample is too big, a rather large loss of energy of the reflected beam may occur. If a filler substance located using the microscope cannot be identified with this equipment it is necessary to apply a more localised analysis with micro-FTIR or Raman micro-spectroscopy.

*FTIR spectra of fissure fillers in emeralds:* Untreated emerald from any natural source shows total absorption below  $2400\text{ cm}^{-1}$  and above  $3400\text{ cm}^{-1}$  with a transmission window between  $2800$  and  $3100\text{ cm}^{-1}$  (Figure 11). The spectra are, however, influenced by the crystal orientation of the emerald (Figure 13). Therefore, tests have been carried out to define the best orientation for recording spectra of treated emerald. A more detailed description of the influence of emerald orientation on FTIR spectra will be given in a later article (Chalain *et al.*, in preparation).

As shown with pure substances, the FTIR spectra of emerald fillers present two characteristic areas which can be used for identification. The best absorption region for organic substances such as C-H groups and cyclic aromatic substances is between  $1700$  and  $1600\text{ cm}^{-1}$ . However, the emerald spectrum shows complete absorption in this region and cannot be investigated. The second characteristic region for filler substances lies between  $2800$  and  $3100\text{ cm}^{-1}$ , in which emerald shows an absorption minimum. Therefore, this region is suitable for analysis. When an FTIR analysis is performed on a treated emerald, a combination of the absorption spectrum of the filler substance and the emerald spectrum is obtained (Figure 11).

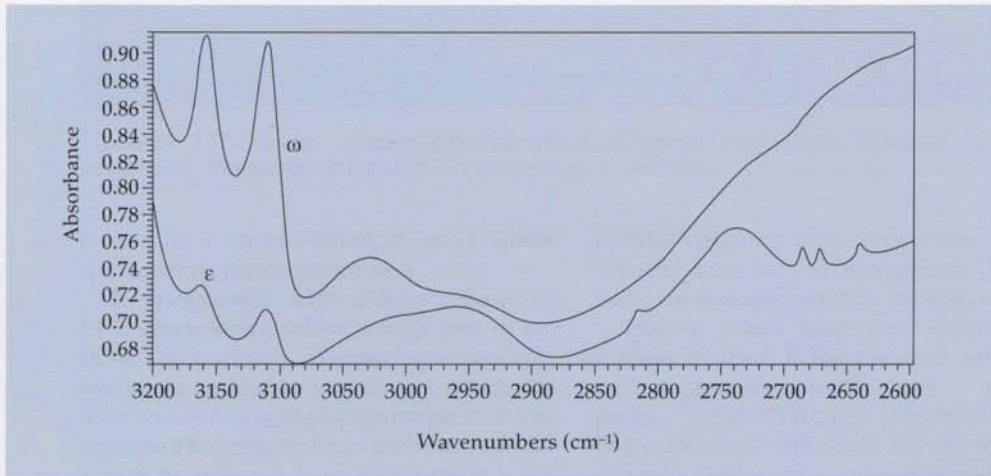
Emeralds treated by one of the authors (HH) with known substances showed that none of the emeralds treated with oil possess any absorption between 3000 and 3100  $\text{cm}^{-1}$  (Figure 14a), while all emeralds treated with various artificial resins do show characteristic absorption features in this region (Figures 11,14b,c). Emerald treated with Canada balsam has yet another typical feature which makes it distinguishable from emeralds treated with other substances. Based on these results, FTIR spectroscopy enables distinction between emeralds treated with oil, with artificial resin, or with Canada balsam. The study was continued by including various treated emeralds with newer substances, which were sent to the laboratory for scientific analysis. Two emeralds were sent to the SSEF laboratory by A. Groom, who promotes emerald treatment with his substance called 'Gemtrat'. Unfortunately the pure substance was not supplied. The FTIR spectra of the analysed stones show features similar to those of epoxy resins, so that the substance can be classified in the group of artificial resins (Figure 14b). Five emeralds donated by R. Giraldo of Colombia, had been treated with 'Permasafe' and a comparison of the spectrum with the solidified substance

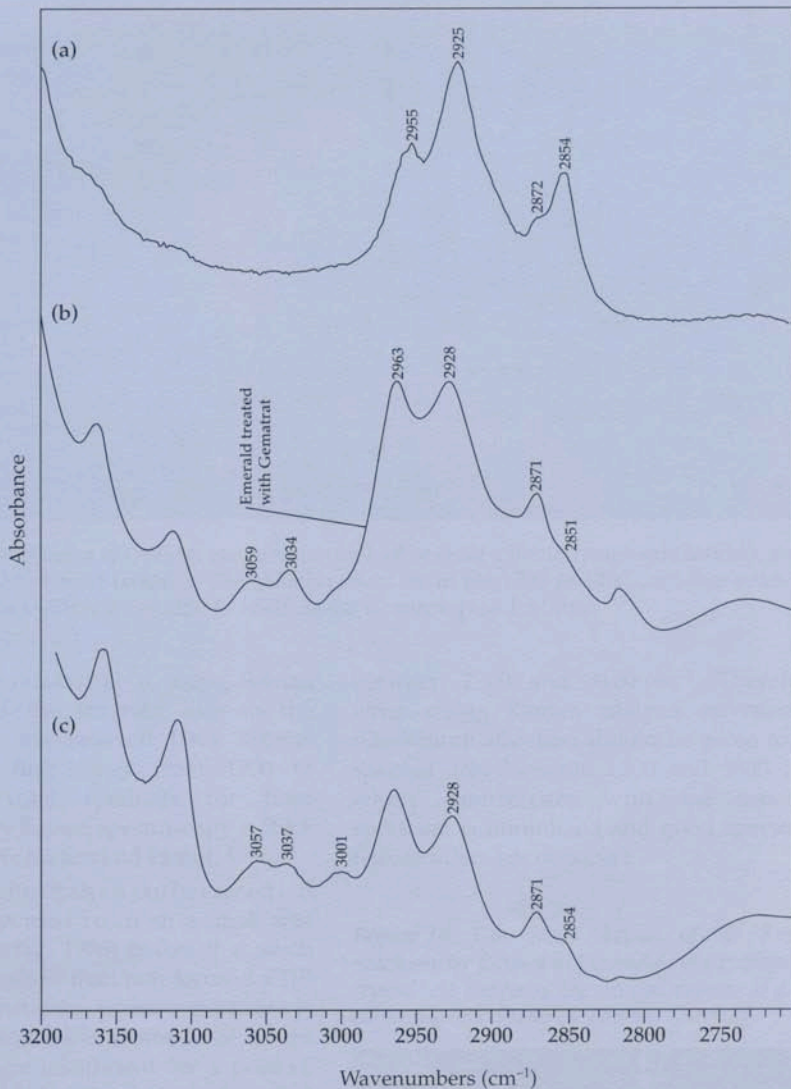
shows good agreement with epoxy resin (Figure 14c). Due to its spectroscopic features, Permasafe is also classified as artificial resin.

When performing FTIR spectroscopy, care has to be taken that no pollutants adhere to the emerald. When the whole stone is analysed by FTIR spectroscopy, such pollutants may disguise a relatively pure stone and may lead to misinterpretation. Among potential pollution sources are the grease from fingers when handling the stone without tweezers, refractometer fluid when the refractive index has been performed before FTIR analysis, or detergent from the water with which the specific gravity of an emerald has been determined. To avoid such effects, care must be taken to clean the emerald thoroughly prior to analysis, preferably with alcohol or acetone.

*Raman micro spectrometry:* The Raman spectrometer is equipped with a microscope for selecting the analytical area and targeting the beam to the selected spot. The advantage of this instrument is the ability to focus inside a sample to several millimetres depth. In this way, gemstone inclusions as small as 2  $\mu\text{m}$  can be investigated (see e.g., Dhamelincourt and Schubnel, 1977; Delé-Dubois *et al.*, 1980; Hänni *et al.*, 1997; Koivula and Elen, 1998), and this makes it convenient to focus into the

Figure 13: FTIR spectra of  $\epsilon$  and  $\omega$  vibrations of emerald show distinct variations in absorbance of OH-bonds within the 'transmission window' between 3200  $\text{cm}^{-1}$  and 2600  $\text{cm}^{-1}$ . © SSEF Swiss Gemmological Institute.





**Figure 14:** FTIR spectra: (a) emerald treated with oil; (b) emerald treated with 'Gemmatrat'; (c) emerald treated with 'Permasafe'. © SSEF Swiss Gemmological Institute.

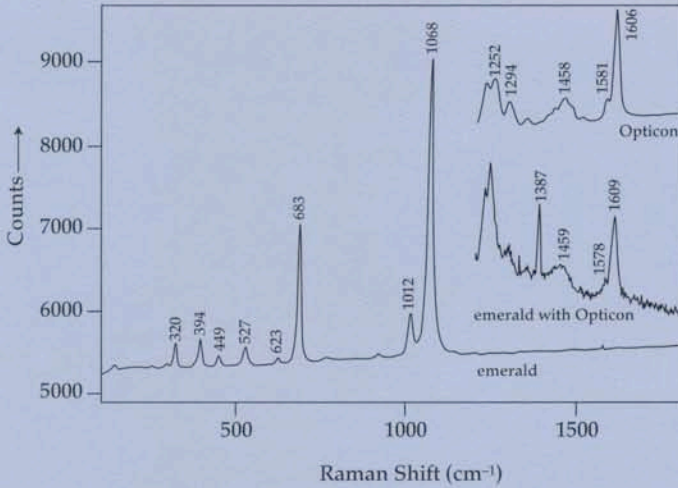
fissure of a fracture-filled emerald where spot analysis can be performed.

In comparison with diffuse reflectance FTIR spectroscopy where a large part of the stone is analysed, Raman spectroscopic analysis is applied to a small spot, which has to be chosen first using a microscope. It is very important to perfectly focus the beam onto the area to be analysed. Even then a result is not

always obtained and very often several different areas have to be analysed. This may make the method very time consuming.

Fissure fillers have two characteristic regions in their Raman spectra which do not interfere with the emerald peaks: 1200–1700  $\text{cm}^{-1}$  (Figure 15) and 2800–3100  $\text{cm}^{-1}$ . Although the second area generally displays more intense peaks than the





**Figure 15:** Raman spectra of Opticon epoxy resin (top), of emerald without treatment (bottom), and of an Opticon-treated emerald (middle). The valuable peaks are in the 1200 to 1800  $\text{cm}^{-1}$  area where the vibrations of organic fillers are visible. © SSEF Swiss Gemmological Institute.

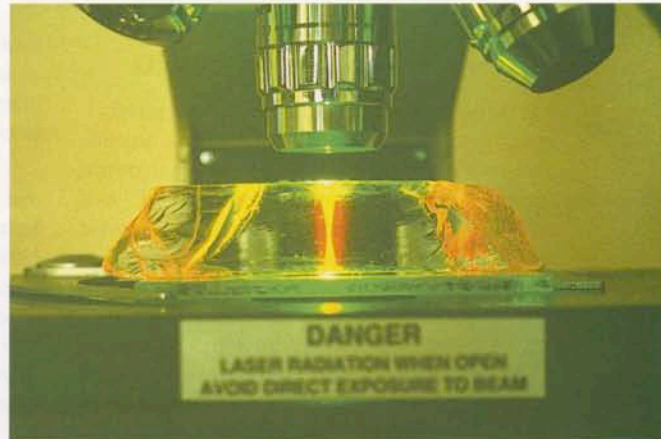
first, it may be masked by a strong Raman fluorescence of the emerald due to the wavelength of the selected laser source. Therefore the first range from 1200 to 1700  $\text{cm}^{-1}$  is used routinely for filler identifications by Raman spectroscopy at SSEF (Hänni *et al.* 1996; Kiefert and Hänni, 1996).

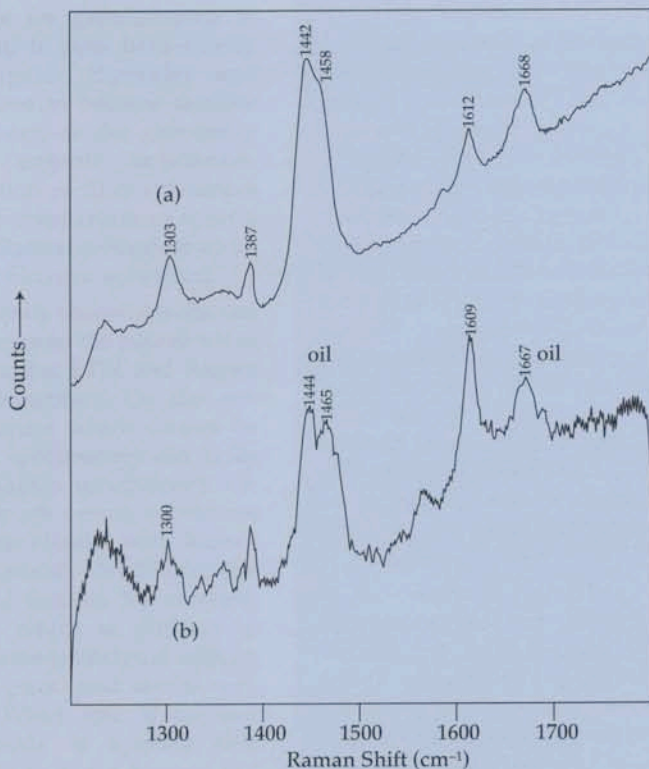
The fact that this analysis can be carried out using a finely focused beam on a small area (Figure 16; Ostertag, 1996) makes it a much more precise method than non-focused FTIR spectrometry. Therefore, where a treatment is visible with microscopic methods or where FTIR analyses are insufficient for a positive identification, the Raman microprobe often supplies a positive response.

*Raman spectra of fissure fillers in emeralds:* as mentioned above, the Raman spectrum of emerald itself shows a number of distinct peaks between 100 and 1100  $\text{cm}^{-1}$  (Figure 15), which are constant for emeralds from many different source areas. Due to the chromium content of an emerald in combination with the selected wavelength of the laser source, the background of the spectrum starts to rise at approximately 2500  $\text{cm}^{-1}$  and increases towards higher numbers. This may mask some of the peaks of the filler substances

between 2700 and 3100  $\text{cm}^{-1}$ . Therefore, when doing Raman analysis on emerald fillers more attention should be given to the spectral area between 1200 and 1800  $\text{cm}^{-1}$  where interference with the emerald spectrum is minimized and good spectra of fissure fillers are obtained.

**Figure 16:** The laser beam of a Raman spectrometer focused in the middle of a transparent crystal. At the focus the excited volume is a few cubic microns. Photo by Thomas Ostertag.





**Figure 17:** Raman spectra: (a) emerald fissure with cedar wood oil; (b) emerald fissure with a mixture of cedarwood oil (1440–65 and 1667  $\text{cm}^{-1}$ ) and artificial resin (1609  $\text{cm}^{-1}$ ). The peak at 1387  $\text{cm}^{-1}$  indicates emerald. © SSEF Swiss Gemmological Institute.

Figure 15 shows the Raman spectrum of an emerald and 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 which, however, is always visible to a certain degree. In contrast, emeralds filled with cedar wood oil show a different spectrum (Figure 17a).

Mixtures of various substances are generally also identifiable. Raman spectra of the more recent 'Gemmatrat' from the United States showed that it possesses spectroscopic properties consistent with a mixture of artificial resin and oil. Multiple fillers which may be the result of incomplete cleaning and refilling with another substance could also show similar mixed substance spectra (Figure 17b).

As in FTIR spectroscopy, care must be taken about any pollution from such sources as dop stick glue.

## Discussion and conclusions

Experience in day-to-day laboratory routine shows that over the past few years identification of fissure fillers in emeralds has been receiving more and more attention in the trade due to new substances being introduced as fillers. The properties of these new substances such as ageing behaviour and removability are generally not well known and those in the trade are concerned about the reversibility of a filling process when the new filler substances are applied.

The identification of fissure fillers presents a challenge for gemmologists in laboratories, who, up to now have mostly specialised in inorganic chemistry and mineralogy. They have to become familiar with organic chemistry, as the commonly used fillers are organic substances. Therefore, identification of filler substances mainly relies on the comparison of spectra obtained by FTIR or Raman methods from an emerald with those of known substances.

As has been frequently observed in the use of mineralogical techniques the experience of the laboratory shows that FTIR and Raman analyses are complementary. On the one hand, certain substances which cannot be identified with FTIR spectroscopy can easily be identified with Raman spectroscopy. On the other hand there are certain substances which are difficult to identify with Raman spectroscopy but are readily identifiable with FTIR. Oil in emerald fissures, for example, shows a spectrum which is difficult to interpret when the same is analysed with an argon ion laser, but gives good results with FTIR spectroscopy. Which one of the two spectroscopic methods is applied first depends on the position of the fissures and the quantity of substance in the emerald.

The identification techniques are complementary to microscopic observations and results obtained by UV light viewing. For an experienced observer, these two latter methods can be used as an indication of a fissure treatment and an estimation of the quantity of filler(s) present.

Using spectral methods for identification, the analyses of filler substances in emeralds may sometimes be difficult to interpret because:

- there may be variations in infrared absorptions of the emerald due to anisotropy, as a function of its orientation;
- more than one filler substance may be present in the interior of the stone which presents a mixed spectrum;
- the fissures may be filled with artificial resins other than epoxy resins (Table I) and may not have aromatic bondings. Continuous research is necessary to keep in contact with developments.

### Synthetic or artificial?

To some people in the trade it makes a big difference if a filler substance is natural or synthetic. They think that a synthetic product is worse and less acceptable. As a matter of fact, synthetic substances (by definition of the term) are analogues to their naturally occurring counterparts. Synthetic cedar wood oil or synthetic Canada balsam for example have basically the same properties as the natural ones. They possess chemical compositions and structures that cause the same optical effects and removability from the stone. Therefore, in the context of emerald treatment it is unimportant to differentiate whether a given substance is in its natural state or duplicated by a synthesis. The characteristics as fillers are the same.

In contrast to this, artificial substances do not have a natural counterpart and are newly designed substances with new properties. Epoxy resins possess chemical structures that were invented and designed by chemists and material scientists. Some of the properties are welcome as emerald enhancers, others are not. The ability to form long molecular chains and to polymerise makes them more durable in some respects, but also difficult to remove once applied. Usually epoxy resins have a refractive index closer to emerald than oils. This makes it hard for the jeweller and goldsmith to evaluate the extent and position of the treatment, and damage may occur during setting. The difference should therefore not be made between natural and synthetic, but between natural and synthetic on one side and artificial on the other.

Recent laboratory experience at SSEF indicates that about 5 per cent of emeralds examined contain fillers which cannot be positively identified. These are generally stones in which the filler has decomposed and become opaque, perhaps losing its original homogeneous chemical characteristics.

## Acknowledgements

The authors would like to thank Dr Michael Krzemnicki, SSEF, for a critical review of the article and for analysing some of the organic substances with Raman spectroscopy, and Mr Peter Giese, SSEF, for analysing the substances with FTIR. C. Abouchas, L. Decque, R. Naftule, A. Sofiov, Th. Färber, D. Piat, R. Nissani, M. Durlabji, K. Scarratt and R. Giraldo supplied us with various commercial filler substances.

## References

- Bosshart, G., 1991a. Emeralds from Colombia (Part III). *Journal of Gemmology*, **22**, 500–3
- Bosshart, G., 1991b. Emeralds from Colombia (Part II). *Journal of Gemmology*, **22**, 409–25
- Chalain, J-P., Hänni, H.A., and Kiefert, L., 1998. Détermination des substances de remplissage dans les émeraudes. In: D. Giard (Ed.), *L'émeraude*. Association Française de Gemmologie, Paris, 107–15
- CIBJO, 1991. *Gemstone Book*. UBOS Bern 120 pp
- CIBJO, 1997. *Gemstone Book*. UBOS Bern, 119 pp
- Delé-Dubois, M.-L., Dhamelincourt, P., and Schubnel, H.-J., 1980. Etude par spectroscopie Raman d'inclusions dans les diamants, saphirs et émeraudes. *Rev. de Gemm. a.f.g.*, **64**, 11–14
- Dhamelincourt, P., and Schubnel, H.-J., 1977. La microsonde moléculaire à laser et son application à la minéralogie et la gemmologie. *Rev. de Gemm. a.f.g.*, **52**, 4
- Epstein, D.S., 1989. The Capoeirana emerald deposit near Nova Era, Minas Gerais, Brazil. *Gems and Gemology*, **25** (3), 150–8
- Federman, D., 1998. Emerald on Trial. *Modern Jeweler*, January 1998
- Fritsch, E., Maitrallet, P., Hémond, G., Lasnier, B., Notari, F., Froyer, G., and Louarn, G., 1999. Première caractérisation du 'Permasafe', nouveau matériaux de remplissage des fractures utilisé pour les émeraudes. *Rev. de Gemm. a.f.g.*, **136**, 44–6
- Gübelin, E.J., and Koivula, J.I., 1986. *Photoatlas of Inclusions in Gemstones*. ABC Verlag, Zürich
- Hänni, H.A., 1988. An oil well in your garden? *Swiss Watch and Jewellery Journal*, March 1988
- Hänni, H.A., 1992. Identification of fissure-treated gemstones. *Journal of Gemmology*, **23** (4), 201–5
- Hänni, H.A., Kiefert, L., and Chalain, J-P., 1996. How to identify fillings in emeralds using Raman spectroscopy. *Jewellery News Asia*, September
- Hänni, H.A., Kiefert, L., Chalain, J-P., and Wilcock, I., 1997. A Raman microscope in the gemmological laboratory. First experiences of application. *Journal of Gemmology*, **25**(6), 394–406
- Hummel, D.O., 1990. *Atlas of Polymer and Plastics Analysis*. 2nd edition. Verlag Chemie, Weinheim, Deerfield Beach, Florida, Basel
- Hurwit, K.N., 1989. Gem trade lab notes. Emerald with plastic-like filling. *Gems and Gemology*, **25**(2), 104
- Johnson, M. et al., 1998. How to detect clarity enhancement in emeralds. *Modern Jeweler* January
- Kammerling, R.C., Koivula, J.I., Kane, R.E., Maddison, P., Shigley, J.E. and Fritsch, E., 1991. Fracture filling of emeralds. *Gems and Gemology*, **27** (2), 70–85
- Kammerling, R.C., Maddison, P. and Johnson, M.L., 1995. Gem trade lab notes. Emerald with unusual flash-effect colours. *Gems and Gemology*, **31**, 1, 54
- Kane, R.E. 1990., Gem trade lab notes. Emerald with filled fractures. *Gems and Gemology*, **26**(1), 95–6
- Kazmi, A.H., and Snee, L.W. (eds), 1989. Emeralds of Pakistan. *Geology, Gemology and Genesis*. Van Nostrand Reinhold, New York
- Kiefert, L., and Hänni, H.A., 1996. Detection of fissure fillings in emeralds using a Raman Microscope. Proceedings of Second Australian Conference on vibrational spectroscopy, Queensland University of Technology, 73–4
- Koivula, J., Kammerling, R.C., Fritsch, E., Johnson, M.L., and DeGhionno, D., 1994. Gem News. New emerald treatment/polishing systems from Israel. *Gems and Gemology*, **30**(2), 122–32
- Koivula, J.I., and Elen, S., 1998. Barite inclusions in fluorite. *Gems and Gemology*, **34**(4), 281–3
- Laskovenko, A.F., and Zherakov, V.I., 1995. An update on the Ural emerald mines. *Gems and Gemology*, **31**(2), 106–13
- Moenke, H., 1962. Mineralspektren. (Aufgenommen mit dem Jenaer Spektralphotometer UR 10). Akademie-Verlag, Berlin
- Nassau, K., 1984. *Gemstone Enhancement*. Butterworths, London 221 pp.
- Nelson, J.B., 1993. The glass filling of diamonds. Part 1. An explanation of the colour flashes. *J. Gemm.*, **23**, 461–72
- Ostertag, T., 1996. Spezielle Anwendung der Raman-Spektroskopie in duen Gebieten der Mineralogie, Petrologie und Gemmologie. Diplomarbeit, Freiburg im Bressgau
- Ringsrud, R., 1983. The oil treatment of emeralds in Bogota, Colombia. *Gems and Gemology*, **19**, 149–56
- Schmetzer, K., Kiefert, L., Bernhardt, H.-J., and Beili, Z., 1997. Characterization of Chinese hydrothermal synthetic emerald. *Gems and Gemology*, **33**(4), 276–91
- Sadtler Research Laboratories, Inc., 1973. *Minerals. Infrared Grating Spectra*. Sadtler Research Laboratories Inc., Philadelphia
- Shida, J., 1991. Enhanced emeralds: how it must be dealt with. *JCA Gems News*, Hawaii meeting, lecture and abstract
- SSEF, 1998. Standards and Applications for Diamond Report, Gemstone Report, Test Report. SSEF Swiss Gemmological Institute Basel. 120 pp
- Themelis, T., 1990. Oiling emeralds. *Cornerstone* 21, 24 July
- Zimmermann, J.L., Giuliani, G., Cheilletz, A. and Arboleda, C., 1997. Mineralogical significance of fluids in channels of Colombian emeralds: a mass-spectroscopic study. *International Geology Review*, **39**, 425–37