Fig. 1: A Colombian emerald mounted with diamonds in a ring, representing the finest 'Gota de Aceite' (oil drop) material in the market. (Photo by T. Hainschwang)

Standards and Protocols for Emerald Analysis in Gem Testing Laboratories

By Dr. Thomas Hainschwang and Franck Notari

The analysis of emeralds – or a stone presented as an emerald – at a gem testing laboratory, requires strict standards and protocols in order to ensure consistent and accurate results. While the mere identification of the stone is part of the procedure, the most demanding tasks are the treatment identification and quantification plus the country of origin determination. The treatment and country of origin determination are of great importance in this market since both of them have a significant impact on the value and/or salability of an emerald. As a gem testing laboratory, you therefore have the responsibility of accurately reporting these parameters which permit a client to properly evaluate his stone.

Background Information

Emeralds are among the most valuable of all gems and represent an important part of the colored gemstone market. Emeralds are only very rarely naturally clean, but typically contain numerous inclusions, with fissures being the most common. These fissures can be filled by various substances like oil, wax or resin, in order to reduce their negative effect on the appearance of an emerald. These clarity treatments, also known as clarity enhancements, need to be declared when an emerald is sold.

Many buyers are not only keen on knowing if and how severely an emerald has been treated, but also want to know which filling substance has been used. This is mainly related to the fact that artificial resins have a more severe effect on the appearance than oil or wax, and that artificial resins are frequently polymerized (hardened), hence very difficult to remove from an emerald. Even in non-hardened resins the polymerization can be brought out by UV, for example by exposure to sunlight. Furthermore, since resins usually act as glues, certain resin-treated emeralds cannot be cleaned because they would break into pieces after such cleaning. As a consequence, certain buyers, or even entire markets, do not want resin-treated emeralds while stones treated with oil and wax are acceptable to them.

Another important criterion for many emerald buyers is the country of origin. The reason: historically certain sources have been regarded as the ones producing the best quality stones for specific gemstones. For emeralds, Colombia holds this status of being the source of the best stones. Today, these origin attributes for gemstones are only partly valid, since many other gem-producing regions have been discovered and developed that can produce equally or sometimes even more beautiful gemstones.

While the country of origin does not guarantee that a gem is of superior quality, this 'value adding argument' has remained since its potential interest was outlined and promoted from the 1950s on by Dr. Eduard Gübelin. In consequence, this information was included in the reports issued by the Gübelin laboratory and later also in the reports by other gem testing laboratories.

While for most emeralds this origin determination is still accurately feasible, for other gemstones, such as blue sapphires, it becomes more and more difficult because of the many mining regions worldwide that produce these gems today. The market profits from this clever branding, using country names to sell stones from different origins at different prices, so a sapphire from Kashmir/India will be traded several times higher than a sapphire from Madagascar/Africa of the exact same quality.

In the case of emeralds, this discrepancy between the different origins is far lower, and often even non-existent. Nevertheless, most traders specifically ask for Colombian origin when buying emeralds for example at auction, while very rarely will somebody ask specifically for another origin such as Zambia, Pakistan or Afghanistan, which can also produce equally beautiful emeralds.

In order to establish accurate gemological reports for emeralds a laboratory needs to be well equipped and the staff must to be experienced in emerald testing procedures. The equipment needed to properly analyze emeralds includes a microscope, UV-Vis-NIR spectrometer, infrared spectrometer, luminescence microscope and an EDXRF chemical analysis system. Some labs may use Raman spectroscopy instead of infrared spectroscopy and LA-ICPMS, SIMS or LIBS instead of EDXRF, but for standard testing procedures infrared spectroscopy and EDXRF are generally the methods of choice.

The Four Steps of the Emerald Analysis Protocol

Step One: Gem Identification

The first step to be performed on a green stone submitted as a natural emerald is identification. In the case of a natural emerald, the identification is usually rather easy since natural emeralds typically contain a large range of inclusions and growth features; the microscopic observation of these inclusions and growth features is generally sufficient to distinguish natural emeralds from other gem species, synthetic emeralds and emerald imitations.

While other gems and hydrothermal synthetic emeralds may contain multi-phase inclusions, the appearance of these is very different from what one can find in natural emeralds (Fig. 2, left). Plenty of other inclusions and growth features such as calcite, dolomite, pyrite, biotite, actinolite fibers, growth channels and sometimes 'gota de aceite' growth or growth spirals (Fig. 2, right) aid in the identification of natural emeralds. Other green gems, such as chromiferous and/or vanadiferous materials, including tsavorite or demantoid garnet, tourmaline, diopside or tremolite, exhibit inclusions that are rather distinct to what one finds in natural emeralds, and the same is true for synthetic emeralds and emerald imitations such as glass or YAG.

In case of doubt about the identity of a green stone after microscopic analysis, the two preferred identification techniques used at a properly equipped gem testing laboratory are infrared spectroscopy and Raman spectroscopy, both

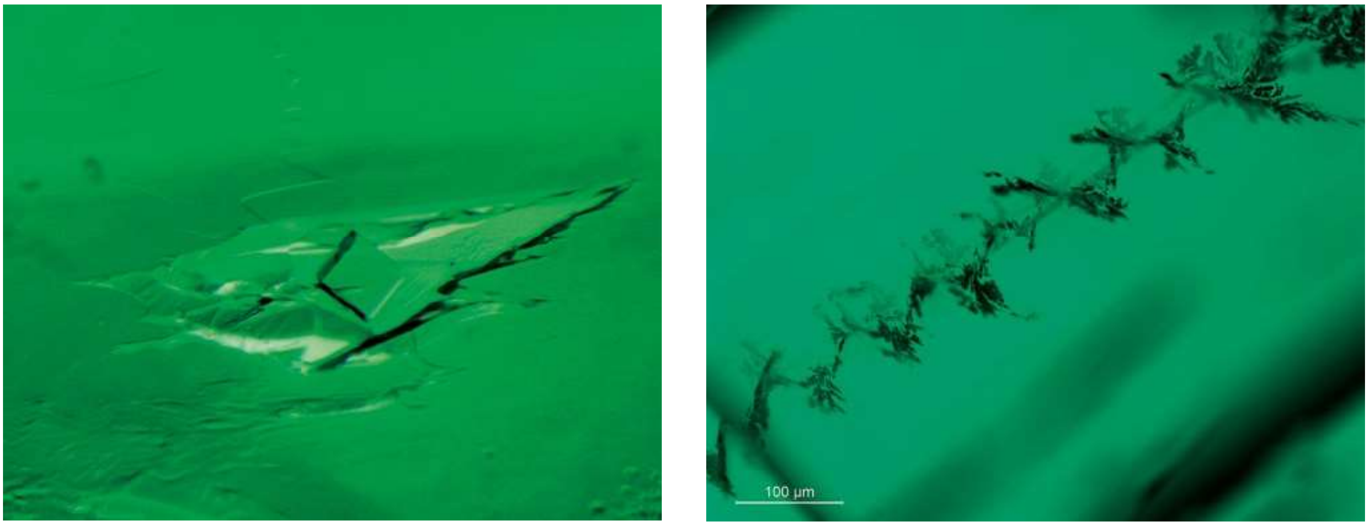


Fig. 2: A quick look in the microscope generally identifies an emerald to an experienced observer. Inclusions like the halite in brine solution with this characteristic jagged appearance (left) and the growth spiral filled by partially dried oil (right) are characteristic of natural emeralds. (Photos by T. Hainschwang)

so-called vibrational methods because they depend on the vibrations of molecules. In infrared spectroscopy the absorption (and transmission) of infrared radiation by a material is measured. With this method, either organic groups detected in materials or the molecular absorption from the material itself can be determined; the absorption spectra are characteristic for the vast majority of materials.

In Raman spectroscopy, a laser is aimed at a material and while almost all the laser light reflected off the material undergoes so-called Raleigh scattering (hence is elastically scattered light found at the same wavelength as the incident laser light), a very small percentage of the laser light is found at a wavelength different from the laser wavelength because of inelastic scattering of the laser light by molecular vibrations. This inelastically scattered light is known as Raman scattering, and most materials exhibit a characteristic Raman spectrum with which the substance can be identified.

While Raman spectroscopy is the method of choice for the identification of inclusions and for certain other specific applications, such as the identification of pigments in pearls, the more versatile and commonly used method for gem identification is infrared spectroscopy. Two different methods are used via different accessories, the first one being with the beam transmitted through a sample via a beam condenser or diffuse reflectance accessory, and the second one being with the beam reflected off the surface of a sample via a specular reflectance accessory.

The second method, specular reflectance infrared spectroscopy, is the preferred technique for gem identification: it identifies the structural absorptions of a material, and therefore enables the identification of virtually any gem material if a proper search database is used. Exceptions are most metallic substances and monoatomic substances, such as diamonds, since they lack a change in dipole moment. Transmission infrared spectroscopy is mainly used for the identification of OH-related species in gem materials and the presence of organic materials such as oil, wax resins or other polymers that are used for treatments.

In the case of the identification of a potential natural emerald, reflected infrared spectroscopy will be used to identify the gem species, hence emerald or not emerald (Fig. 3) and if there is a doubt that the emerald is natural or synthetic, then transmission infrared spectroscopy is one of the methods that can help in solving the problem rapidly (Fig. 4 and 5). As seen in Fig. 3, the bands detected in emeralds are very distinct from other green materials. Since they are identical in natural and synthetic emeralds, this method cannot be used to distinguish them.

Synthetic emeralds are grown either from an anhydrous melt in the so-called flux synthesis, or in a hydrous solution in the so-called hydrothermal synthesis. Flux grown emeralds are very rapidly identified because they lack water-related

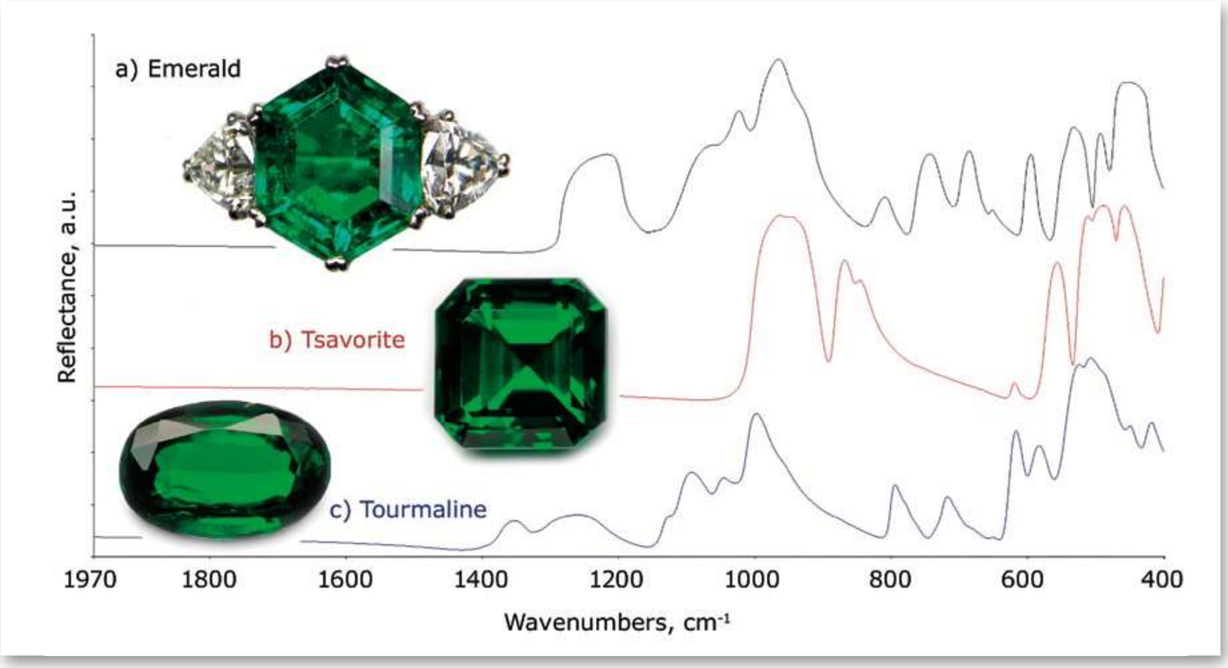


Fig. 3: The reflected infrared spectra of various green gemstones demonstrate how easily they can be distinguished from each other via this method. (Photos by T. Hainschwang)

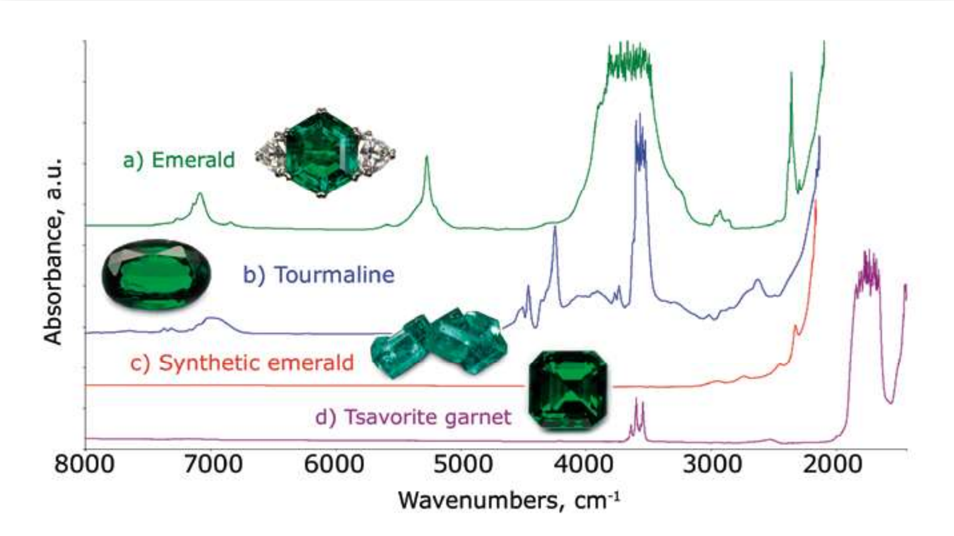
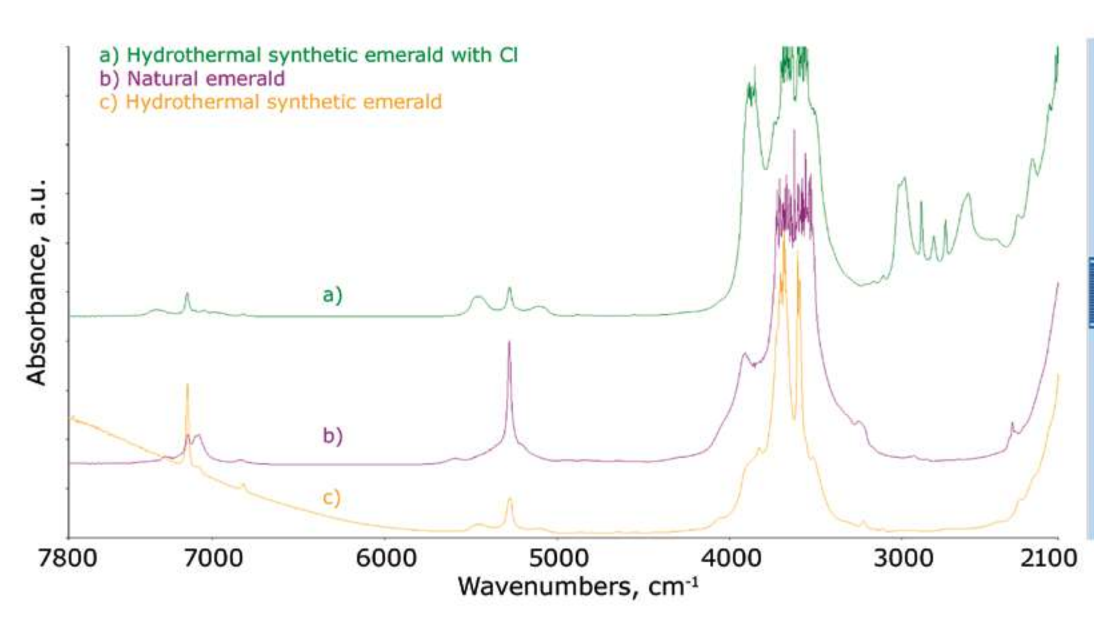


Fig. 4: While transmission infrared spectroscopy also enables a user to distinguish many gem species, this method is more typically used for the identification of filler substances. In the case of emeralds, it both identifies a clarity enhancement and distinguishes natural (trace a) and flux synthetic (trace c) emeralds. Photos by T. Hainschwang.

Fig. 5: Transmission infrared spectroscopy is one of the techniques used for the distinction of natural (trace b) and hydrothermal synthetic (traces a and c) emerald.



absorption in their infrared spectra (Fig. 4, trace c), while natural emeralds show very strong water-related bands (Fig. 4, trace a). This technique can also be used to identify other gem species based on their OH absorptions, but this is more rarely applied because of very variable intensities and possible overlaps of these absorptions from gem to gem.

Hydrothermal synthetic emeralds do contain water and their IR spectra bear quite some similarity to natural emeralds, but looking at the details of such spectra these synthetics can easily be identified (Fig. 5). This can be done from the observation of specific absorptions, such as chlorine-related peaks present in some hydrothermal synthetics, or deuterated water peaks that are characteristic of natural emeralds.

Step Two: **Treatment Identification**

It is a well-known fact that virtually all emeralds often contain numerous open fissures. These fissures are often filled with some type of filler that has a refractive index close to that of an emerald. Generally, before going to spectroscopic methods, a glance under the microscope will reveal whether any fissures in an emerald are empty or if they have been filled.

Under brightfield illumination, fissures filled by an epoxy resin (which is essentially a glue) with a refractive index very close to emerald exhibit an interference effect known as the flash effect, where orange, pink and blue colors are visible along the flashes (Fig. 6). Oil- and wax-filled fissures only rarely show a weak flash effect, hence this observation is a good indication that a stone has been resin treated.

The traditional fluorescence examination of the filler substances is also a good indicator for a basic distinction between oil/wax and resins: most oils and waxes luminesce more yellowish under longwave UV and violet to blue light, while resins luminesce more whitish/bluish under such excitations (Fig. 8). This said, the test is not recommended, because the UV light can induce polymerization of epoxy resin making the cleaning of a stone very difficult, or even impossible.

These enhancements substances can be conclusively identified either by Raman spectroscopy or by infrared spectroscopy. Of these two methods, infrared is typically the preferred method because it enables not only the identification of one specific point in a single fissure at a time like the Raman does, but the result is a more representative one since many fissures and larger surfaces are tested at the same time. The large transmission window in the infrared spectrum at around 3,000 cm-1 is the domain where characteristic peaks of filler substances can be found (Fig. 7).

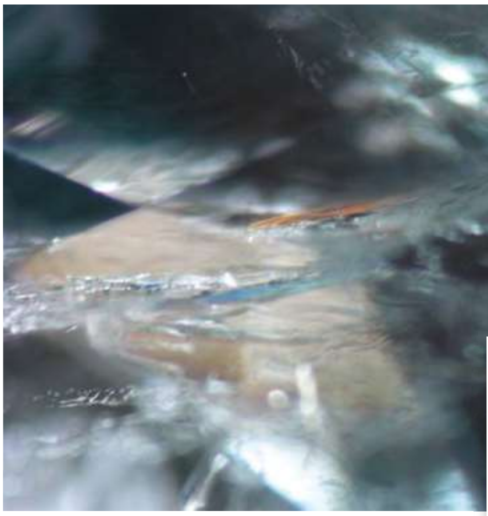


Fig. 6: The orange-blue colored flash effect as seen in the fissures of a resin treated emerald. (Photo by T. Hainschwang)

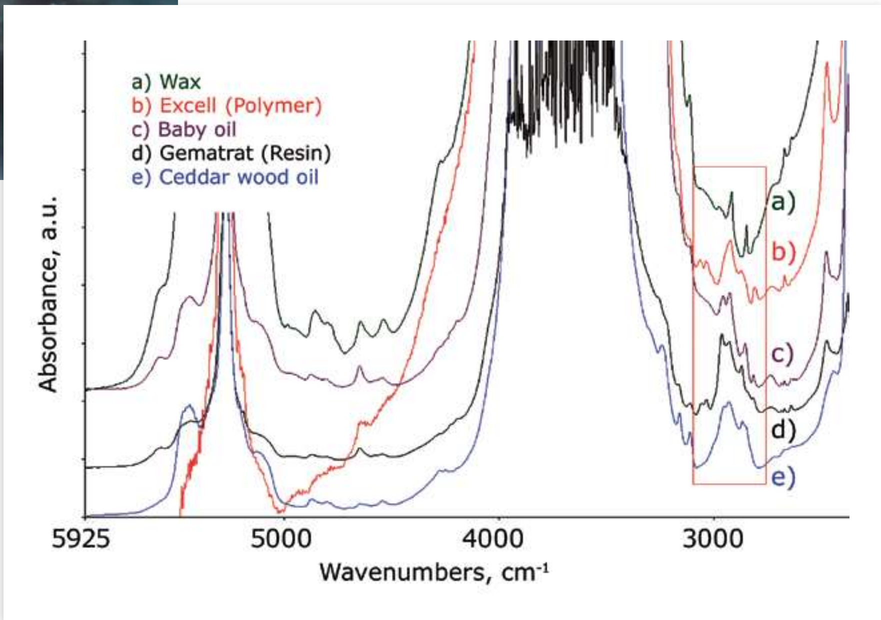


Fig. 7: The transmission infrared spectra of emeralds treated with different substances in order to reduce the visibility of surface-reaching fissures. The various substances can be identified by the spectral signature in the transmission window from 3,100 to 2,800 cm-1.

This method is very efficient for the identification of substances, but has some limiting factors: when there is only a very low quantity of a filler present in a stone, then the signal is very weak, and it may be a delicate issue to conclusively identify a substance, especially when mixtures of several substances have been used. Such mixtures of oil and resin, for example, can be very tricky to identify because the dominating substance can mask the spectral signature of the other substance and in such cases, the conclusions must be established by a very experienced technician.

The intensity of the spectral signal of the filler substance can give a first indication of how significant the degree of enhancement is, but even with several spectra recorded with the IR beam taking different paths through the sample this technique is generally not satisfactory to quantify the treatment.

Step Three: **Clarity Treatment Quantification**

During analysis of an emerald, the observation of the appearance and the quantity of surface-reaching fissures combined with the data obtained via infrared spectroscopy can give a relatively good idea about how severely an emerald has been treated. Typically, the amount and depth of surface reaching fissures linearly correlates with the severity of the clarity enhancement. It must be mentioned, though, that this type of approximation is not precise at all, especially in resin treated stones, since the extent of some fissures is difficult to estimate.

The only proper way to get an acceptable approximation

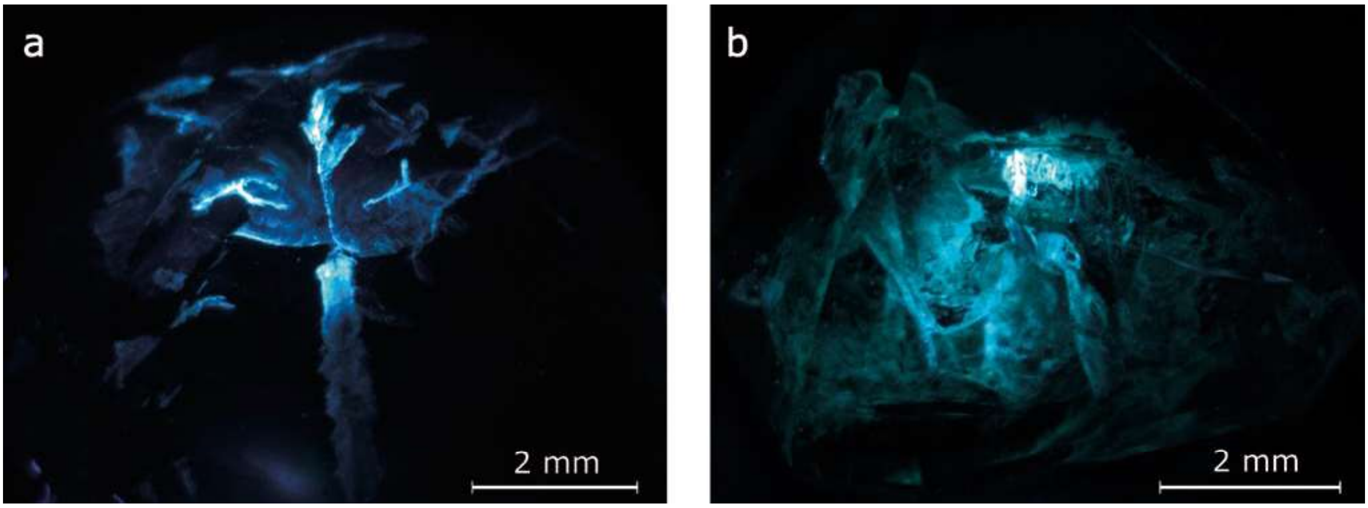


Fig. 8. The DFI luminescence images of two clarity-enhanced emeralds; on the left by an epoxy resin and on the right by oil. The luminescence color is indicative of whether oil/wax or an epoxy resin has been used. The extent of luminescing fissures gives a good quantitative approach to the treatment. (Photos by T. Hainschwang)

of the severity of the enhancement of an emerald is via luminescence techniques. The filler substances all luminesce under intense UV and blue light excitation; under regular (and hence rather weak) UV lamps some oils may appear inert. In order not to further polymerize a filler substance, it is recommended to use light in the blue spectral range instead of UV to bring about the luminescence.

At the GGTL laboratories, this is done using specialized luminescence microscopes – such as the DFI Laser+ luminescence microscopy and spectroscopy system or the U-Visio System – that were developed by us for specific gem testing tasks such as diamond sorting and emerald clarity enhancement testing.

Based on the amount of luminescing fissures that can be seen in an emerald (Fig. 8), combined with microscopic and infrared spectroscopic testing, an appropriate estimation of the degree of enhancement can be given. It must be kept in mind that in the most experienced gem testing laboratories, it is not the amount of filler that is indicated, but rather the degree of enhancement is expressed. This conclusion – even though based on clear scientific evidence – only represents an opinion, since nobody actually knows to what degree the appearance of an emerald has been enhanced through such a treatment.

The only way of actually knowing this with certainty is to clean an emerald using appropriate solvents; at the GGTL Laboratories we perform emerald cleaning and re-oiling with natural cedar wood oil, hence we do know what type of negative surprises one can sometimes have when emeralds that were considered to have only 'minor clarity enhancement' have been cleaned. Also, the nomenclature typically used for the quantitative indication of the treatment – none, minor, moderate, significant (plus insignificant by some laboratories) – cannot be standardized. One can only attempt to use a similar approach between all laboratories, but in reality it must be expected that a difference of one grade can occur when a stone is sent to different laboratories.

Step Four: **Geographical Origin Determination**

As mentioned in the introduction, the geographical origin determination is of surprisingly great importance in today's market and for many gems – including emeralds – this information is considered either a value-adding factor or positive for the salability of a gemstone. While for certain gemstones the geographical origin determination is more and more problematic (especially for blue sapphires), for emeralds this information can usually be determined with very high probability. Nevertheless, it must be kept in mind that origin determination represents only an opinion – not proof – based on the analytical data collected.

The determination of the geographical origin of emerald is based on a combination of microscopic observation of inclusions and growth features, infrared and UV-Vis-NIR spectroscopic analysis, chemical analysis by either non-destructive X-ray fluorescence spectroscopy (EDXRF) or more rarely (being destructive methods leaving small craters) mass spectroscopy such as LA-ICPMS or SIMS or atomic emission spectroscopy such as LIBS, and finally

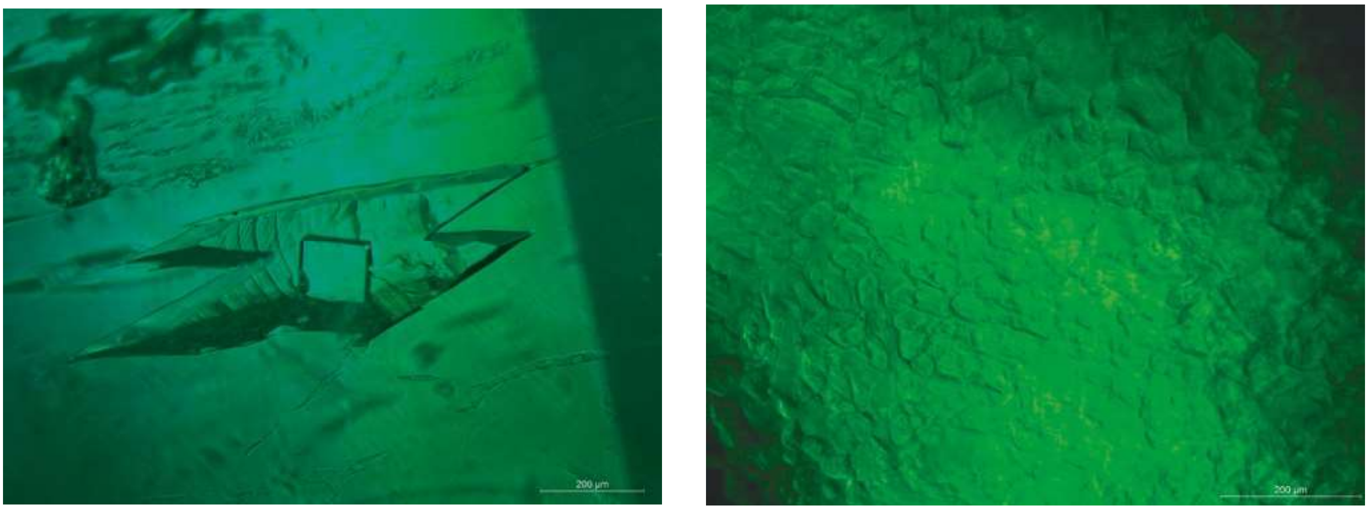


Fig. 9: Typical inclusions/growth features in emeralds from Muzo/Columbia. On the left, a jagged multi-phase inclusion; while, right, very distinct 'gota de aceite' growth structure. (Photos by F. Notari (left) and T. Hainschwang (right))

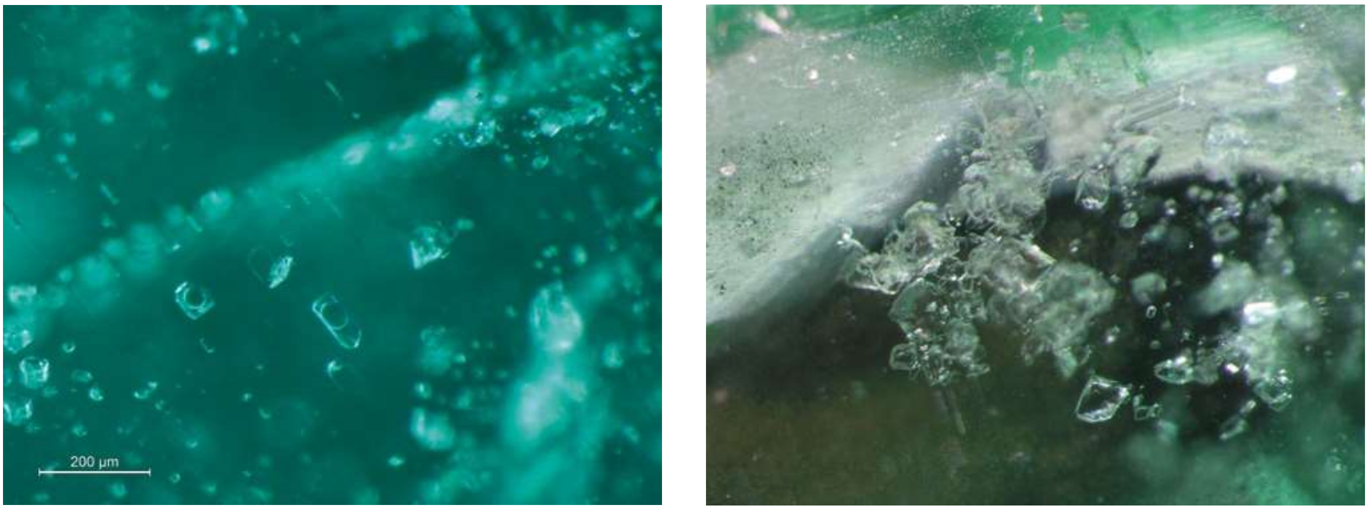


Fig. 10: On the left, multi-phase inclusions in an emerald from Itabira/Brazil; right – dolomite inclusions in an emerald from Santa Terezinha de Goiás, Goiás/Brazil. (Photos by F. Notari (left) and T. Hainschwang (right))

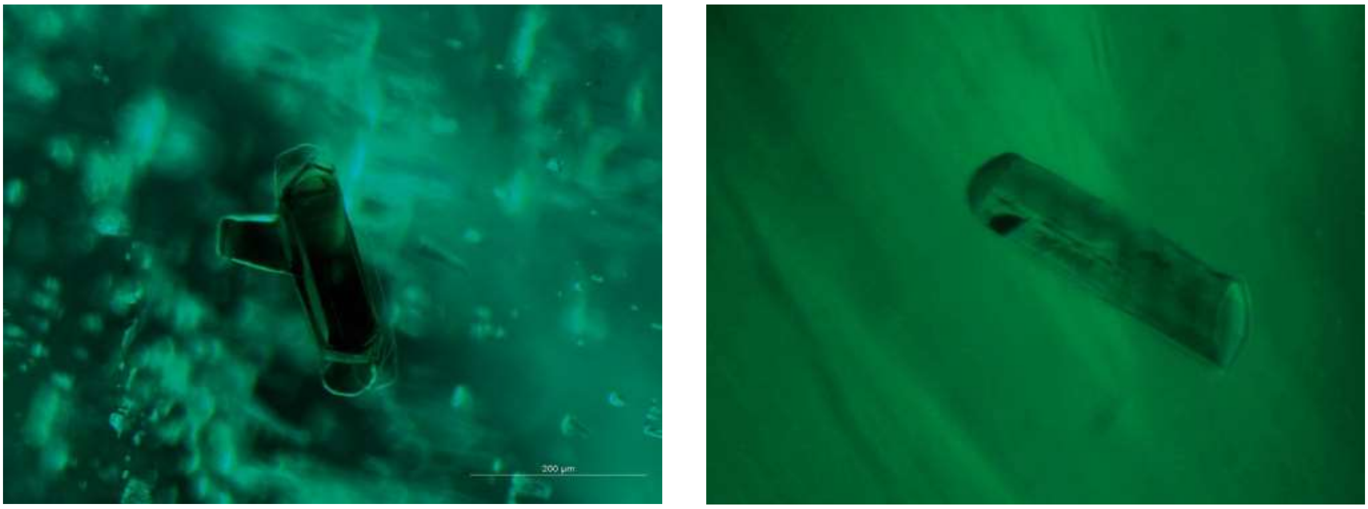


Fig. 11: Left – Phlogopite mica inclusion in an emerald from Kafubu/Zambia; right – Chrysoberyl inclusion in an emerald from Kafubu/Zambia. (Photos by F. Notari)

even photoluminescence spectroscopy. In some cases, the inclusions and growth features alone are sufficient to declare a geographical origin for an emerald, but for many stones further in-depth testing must be performed.

The microscopic observation of inclusions and growth features is perhaps the most important technique for geographical origin determination. Depending on their growth environment (i.e. schist type emeralds VS non-schist type emeralds), emeralds contain different types of inclusions. The mineral inclusions present are a mirror of the minerals that are found in the emerald host rock. To give a prominent example, emeralds from the Muzo region of Colombia are found in black shales accompanied by mainly calcite/dolomite/quartz/pyrite and parasite and in consequence these minerals are frequently found as inclusions in such emeralds.

Multiphase inclusions (i.e. inclusions consisting of more than one phase) can be found in emeralds from different origins, but jagged shaped three-phase inclusions consisting of a liquid phase (brine), a gas bubble and a solid phase – usually a halite (NaCl) crystal – are usually from Colombia (Fig. 9, left). A growth structure that can only be found in emeralds from the Muzo area in Colombia is the so-called 'gota de aceite' structure. As indicated by the Spanish name, the interior of such emeralds appears as if it is full of oil drops (Fig. 9, right).

In Figs. 10 and 11, some inclusion images of Brazilian and Zambian emeralds can be seen, and demonstrate how different these origins are from each other.

When the microscopic observation of inclusions is not sufficient for geographical origin determination, then a combination of spectroscopic and chemical testing is used. From the methods available, some details of chemical testing and UV-Vis-NIR absorption spectroscopy are given in the following section.

Chemically, the most important elements compared between emeralds from the different origins are chromium, vanadium, iron, gallium, scandium and cesium and sometimes rare earth elements. Most emeralds from Colombia have a very low iron content and high chromium and vanadium content, while many other deposits that are commercially important produce emeralds with much higher iron content and typically much more chromium than vanadium; emeralds from Kafubu/Zambia are examples for such iron-rich emeralds.

These distinct chemical differences can be seen directly in the UV-Vis-NIR spectra of emeralds. In figures 12 and 13, the polarized spectra of emeralds from the two above-mentioned origins are shown, and it is obvious that the spectral data is distinctly different: the spectra of a high V/Cr and low Fe containing emerald from Colombia is shown in Fig. 12 while the spectra of an emerald from Kafubu/Zambia with high Fe and relatively low Cr (plus very low V) content are shown in Fig. 13. While the Colombian emerald spectra are characterized by strong Cr^{3+}/V^{3+} absorptions and a lack of distinct Fe^{2+} and Fe^{3+} absorptions, the spectra of the emerald from Kafubu/

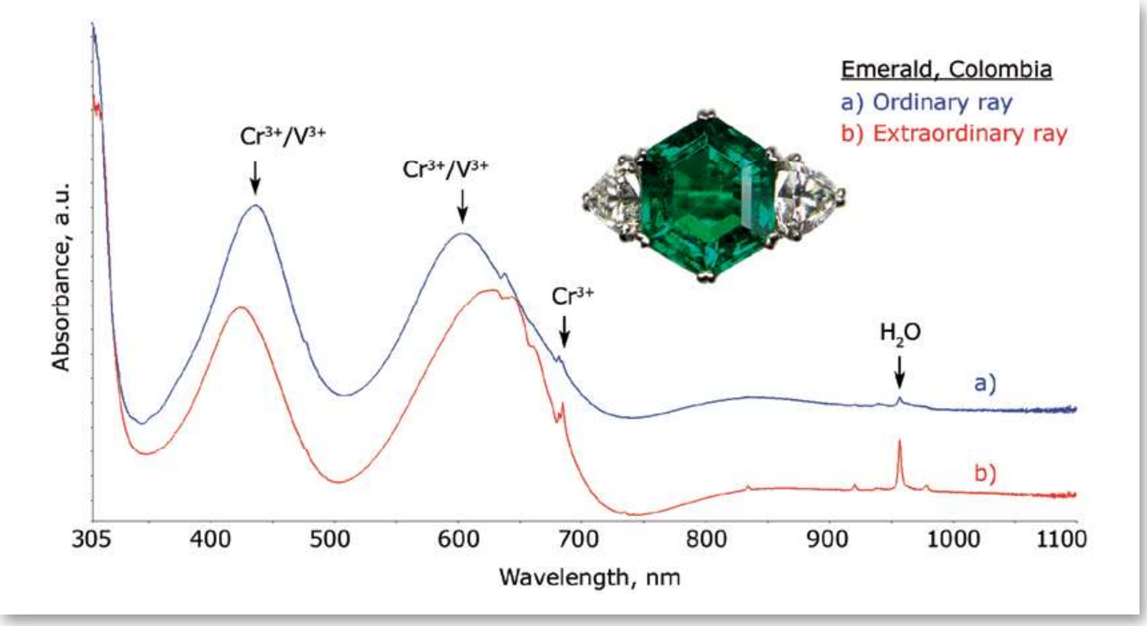
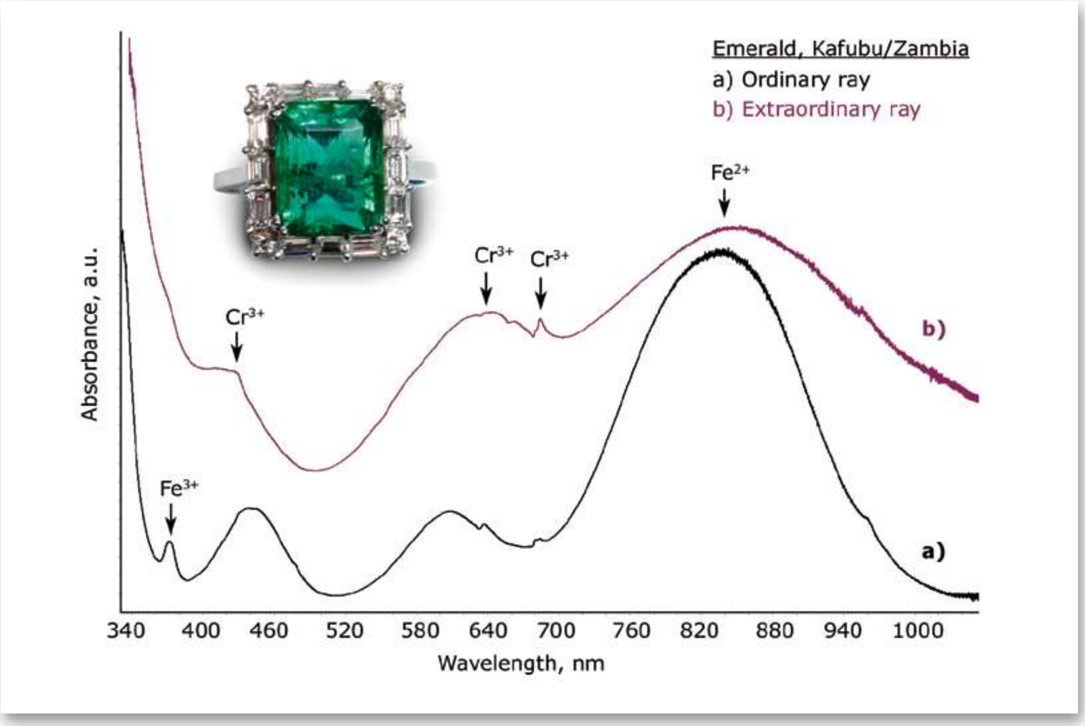


Fig. 12: The polarized UV-Vis-NIR spectra of a Colombian emerald rich in V^{3+}/Cr^{3+} but very poor in Fe^{2+}/Fe^{3+}. (Emerald photo by T. Hainschwang)

Fig. 13: The polarized UV-Vis-NIR spectra of an emerald from Kafubu/Zambia rich in Fe^{2+}/Fe^{3+}, but comparatively poor in Cr^{3+} and very poor in V^{3+}. (Emerald photo by T. Hainschwang)



Zambia exhibits very strong Fe^{2+} and distinct Fe^{3+} absorption combined with comparatively weak Cr^{3+} absorptions.

Discussion and Concluding Remarks

The analysis of green stones submitted as emeralds consists of four steps: 1) gem identification, 2) treatment identification, 3) treatment quantification and 4) geographical origin determination.

While it can be assumed that the analytical protocol is very similar from laboratory to laboratory (providing the labs having similar equipment), the definition of standards is still problematic: for emeralds the most arbitrary judgment is the quantification of the clarity enhancement. While this judgement depends on roughly the quantity and importance of filled fissures, such a judgement is rather subjective: it is impossible to standardize limits between the different grades since there are too many possibilities and parameters that influence the effects of fissures on the appearance of an emerald.

Even the definition of the grade “none” is problematic, since in many emeralds minute residues from the cutting process can be found; these have no positive influence on the appearance of an emerald, but are often declared as “minor” enhancement. It is difficult, or even impossible, to distinguish such ‘pollution’ from a real treatment.

Other difficulties include the identification of the filler substance when very low quantities of a filler are present and when mixtures of fillers are used. And last, but not least, some origins may be difficult to distinguish from each other, such as some of the schist-type emeralds that are mainly characterized by a content of Fe>>Cr>>V, mica and actinolite inclusions as well as relatively simple multi-phase inclusions.

In conclusion, while the major and properly equipped laboratories are all trying their best regarding the proper analysis of emeralds, one must keep in mind that some of the criteria that need to be identified cannot be standardized or are, to a certain degree, based on the opinion of the analyst and not only on scientific evidence. Hence it is possible that the results of a specific stone may vary to a certain degree from laboratory to laboratory. ♦

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