How to identify fillings in emeralds using Raman spectroscopy

Raman spectroscopy is being used for the non-destructive identification of organic foreign substances in gemstones, particularly emeralds, by an increasing number of gemmological laboratories around the world.

Picture one: a Renishaw Raman microscope with the laser source behind the spectrometer box. This system is operated at the SSEF Swiss Gemmological Institute in Basel, Switzerland

A typical instrument consists of a microscope, with transmitted or reflected light, a low power laser excitation source, a spectrometer for high resolution light analysis and a computer for data collection and analysis. The system can be placed on a desk top, picture one.

The Raman microscope has a high spatial resolution enabling the 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, and enables the examination of the profile of layered compounds or inclusions in gemstones, with minimal contribution from the main bulk species. The analysis is fast, does not require sample preparation and, most importantly, is non-destructive.

Identifying organic fracture fillings in emeralds

As fissures are common in emeralds, resins, oils or fats are used to enhance the appearance of the stones. The fillers have a refractive index similar to that of emeralds, and they reduce the visibility of the previously air filled fissure planes considerably. Epoxy resins, including Opticon, are among fillers widely used.

Infrared spectroscopy has been the standard method so far for identifying these fillers but identification may be restricted by the small amount of substances in the fractures and the relative intransparency of emeralds to infrared radiation.

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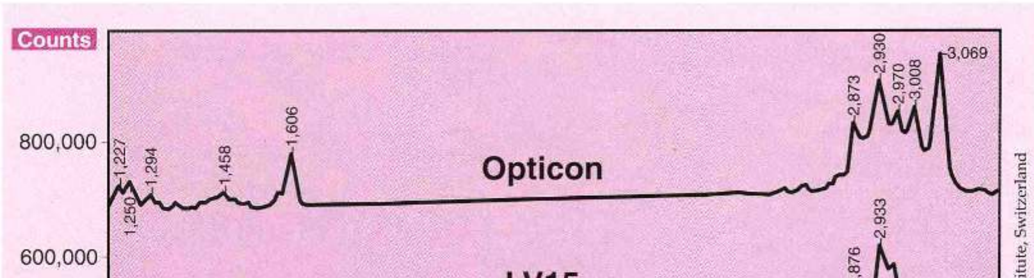
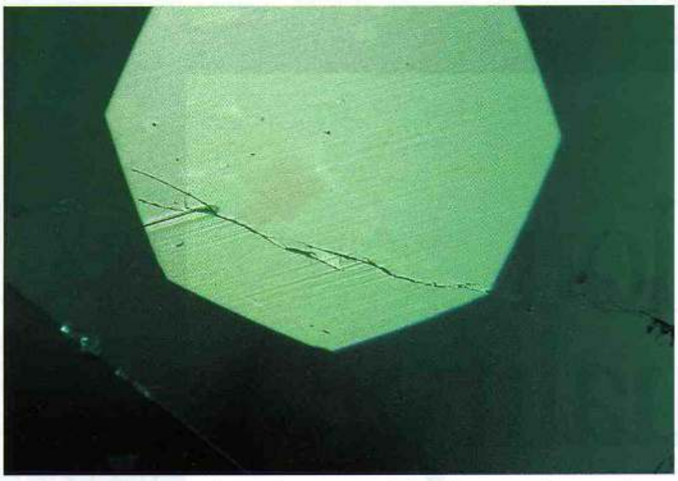
By analysing the scattering of light on molecules which are hit by a monochromatic light beam producing characteristic spectra for different materials, the Raman microscope enables the identification of the various organic fillers due to their different molecular structures.

The main spectral information in the Raman spectra of natural and artificial oils or resins appears in the region of 2,800 cm^{-1} to 3,100 cm^{-1}, another spectral section with characteristic peaks is between 1,200 cm^{-1} and 1,700 cm^{-1}, picture two. The picture

continued on page 156



Picture two: Raman spectra of organic substances commonly used to fill fractures in emeralds. The spectrum of the artificial epoxy resin, Opticon, shows distinct differences from the other substances



Picture three: surface of an emerald with open fracture in reflected light

Picture four: extension of the fracture into the stone. Fracture filling becomes visible due to partial dark field illumination

Raman spectroscopy

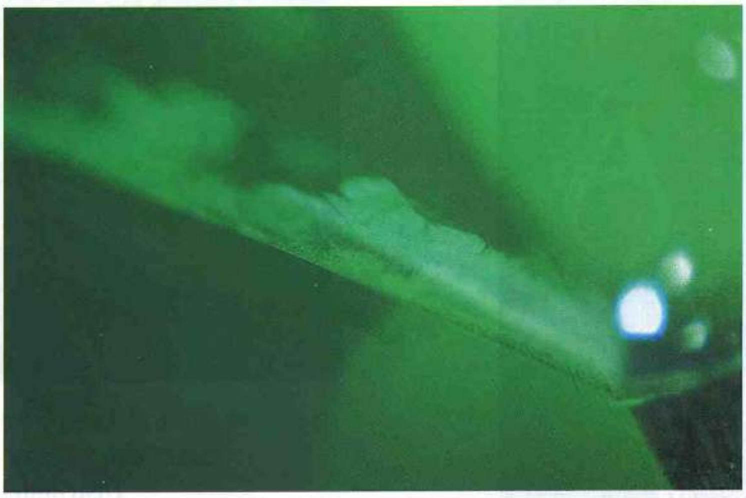
shows the Raman spectra of three substances frequently used as fracture fillers in emeralds. Most important differences between natural and synthetic substances are expressed by the peaks at 1,250 cm^{-1}, 1,606 cm^{-1}, 3,008 cm^{-1} and 3,069 cm^{-1} in artificial resins. These peaks are absent or extremely weak in natural resins or oils.

Preceding the recording of a spectrum is the positioning of the spot to analyse under the microscope, and focusing the laser beam to the area of interest. Picture three shows the surface of an emerald with open fracture, picture four the extension of the fracture into the stone, and picture five the resinous filler in the fracture under magnification. When there is sufficient substance in the fissure, spectra may result as shown in picture six which can be identified by comparison with reference spectra stored in the computer of the system.

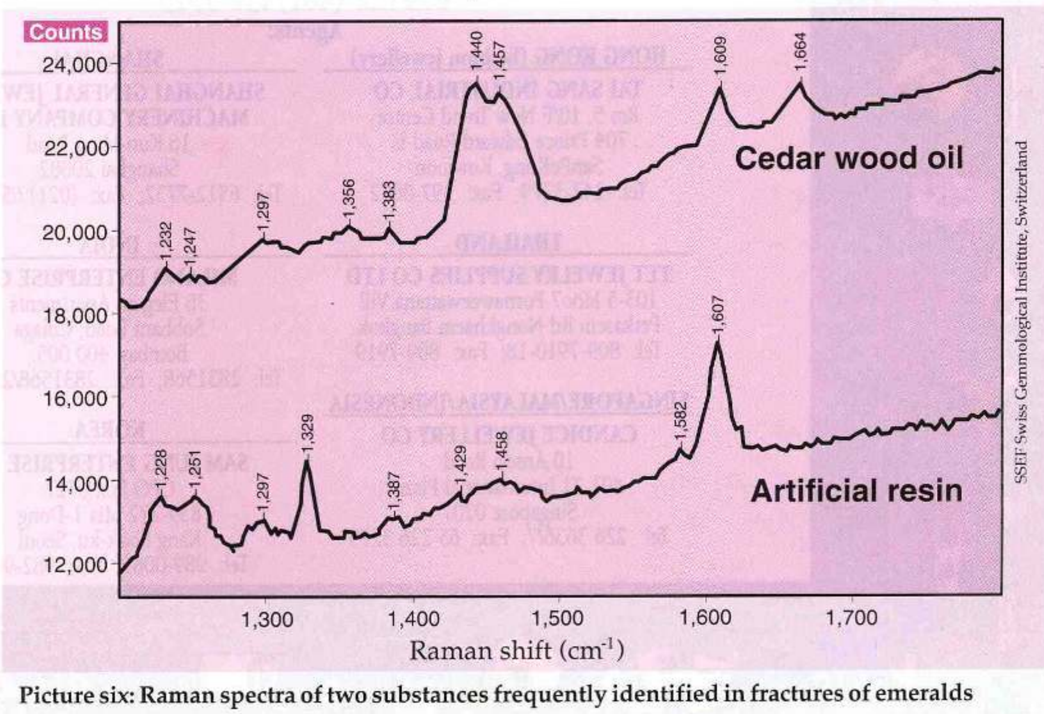
Raman spectra of organic fillers are subject to changes of appearance due to ageing.

Depending on the age and the type of substance, the Raman spectrum will get an additional hump due to fluorescence at 2,800 cm^{-1} to 3,100 cm^{-1}. This fluorescence contribution to the usual spectrum may mask the characteristic lines and identification of an aged substance may not be possible.

Fortunately, the spectral region around 1,500 cm^{-1} is not affected as strongly and still characteristic for identification.



Picture five: resinous filler in the fracture as visible for the Raman analysis



Picture six: Raman spectra of two substances frequently identified in fractures of emeralds