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.

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.

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.
Gemstones

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

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