Application Note: 51123

# Analysis of Emeralds by FT-IR Spectroscopy: Identifying Treated and Synthetic Emeralds

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**Key Words**

- Identifying Simulants
- Identifying Synthetics
- Treatment Detection

## Introduction

Some of the most valuable gemstones are naturally occurring, large, and flawless emeralds of specific colors. Although emeralds are relatively common, the natural process which creates them produces few emeralds that do not contain inclusions, cracks, and other flaws. As with all gemstones, the immense value that can be obtained by improving the appearance of the stone has lead to many processes to artificially enhance quality. Natural oils and waxes have traditionally been used to enhance the appearance of emeralds. More recently, sophisticated techniques have been employed to inject the stones with epoxies or polymers that have the same refractive index as emerald. In some cases, the polymers are colored to match the emerald. While applying a natural oil to the stone is often considered acceptable, treating the stone with refractive matching synthetic polymers is not.

Additionally, there are a number of processes for synthesizing emeralds, the most common of which are hydrothermal and flux. Infrared spectroscopy is a valuable tool for identifying both treated and synthetic emeralds. Emeralds are a member of the Beryl group and are composed of aluminum and beryllium silicates with traces of chrome to create the color. In this application note, we will describe several examples of the use of FT-IR in the analysis of emeralds[1-4].

## Experimental

Excellent infrared spectra can be obtained from emeralds using a Thermo Scientific Nicolet™ 6700 FT-IR spectrometer and either a beam condenser or the Thermo Scientific Collector™ II diffuse reflectance accessory. For emerald analysis, a spectral resolution of 4 $cm^{-1}$ is adequate. The measurement time is dependent upon the infrared detector and the amount of signal getting through the sample.

Figure 1: Thermo Scientific Nicolet 6700 FT-IR and Collector II accessory showing measurement path through a gemstone

The figure below shows that the beam condenser and the diffuse reflectance accessory provide equivalent information for transparent stones. (These spectra were acquired from a small stone in less than one minute). However, since many emeralds contain inclusions and flaws, the Collector II may be a better choice because it collects more of the diffuse light reflected from the stone.

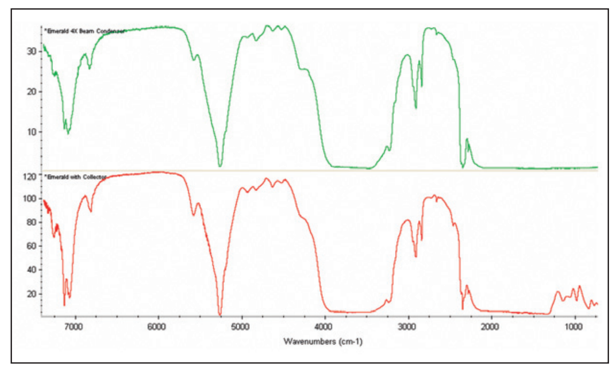


Figure 2: Spectra from a small emerald showing valuable peaks between 5000 and 7000 $cm^{-1}$

The most important spectral region for identifying treated stones is around 3000 $cm^{-1}$. The peaks in this region generally correspond to the C-H bonds in organic compounds. The exact position of these peaks reveals a great deal about the chemical structure of the organic material. The figure below shows an expansion of the absorbance spectrum from the emerald displayed above and a spectrum of a common hydrocarbon oil or wax. The lower spectrum is the result of digitally subtracting the spectral features of the oil spectrum from the emerald. The complete disappearance of the oil peaks clearly indicates the presence of a simple oil or wax.

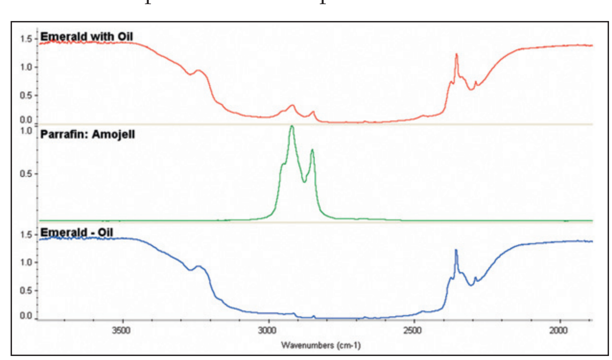


Figure 3: Spectral subtraction of reference oil spectrum from the spectrum of an emerald with peaks suggesting treatment

While it is relatively easy to identify the presence of organic material, it is more difficult to differentiate a natural oil from a polymer. However, the majority of the polymeric materials used in treating emeralds contain aromatic C-H peaks. The figure below shows a comparison of the spectra from the types of material frequently encountered in treated stones with that of paraffin. The highlighted region contains peaks corresponding to aromatic hydrocarbons. Although the presence of peaks in this area is indicative of an epoxy or polymer treatment, certain natural oils such as cinnamon oil also contain a small amount of aromatic CH, making the identification more difficult. A computer match algorithm such as least squares or correlation match can frequently identify the synthetic polymer materials from the aromatic oils that might be considered natural.

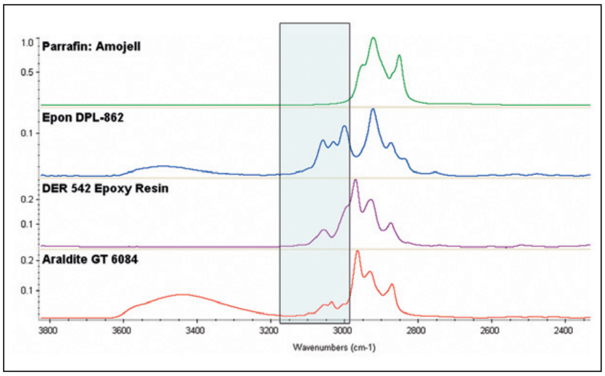


Figure 4: Reference spectra of materials commonly used in treating emeralds

A more challenging task is identifying synthetic emeralds. Natural emeralds contain a significant amount of water and hydroxyl groups (O-H) that can be detected in the infrared spectrum. The figure below compares the spectrum acquired in our laboratory from a green gemstone with a series of spectra kindly provided by Gagan Choudhary of the Gem Testing Laboratory in Jaipur India[5].

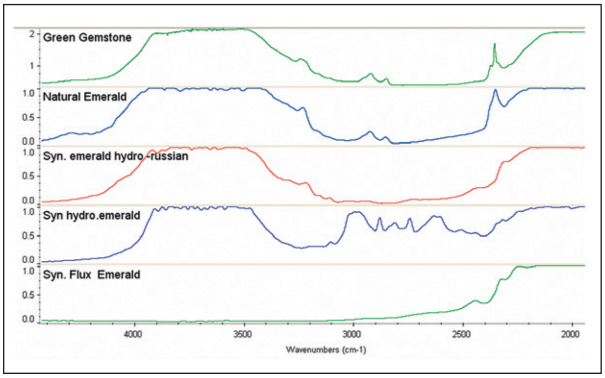


Figure 5: Reference spectra from synthetic emeralds

The comparison of our stone to the natural emerald is very good including the presence of hydrocarbon peaks at 3000 $cm^{-1}$. The emerald created by the flux process shows almost no hydroxyl peaks between 3400 and 4000 $cm^{-1}$. One of the emeralds created by the hydrothermal process shows a number of peaks that have been attributed to the presence of chloride species in the stone. However, the spectrum from the sample created by the Russian hydrothermal process is very similar to a natural stone. There is a peak near 2350 $cm^{-1}$ that appears distinct in natural emeralds and may be an aid in identification.

## Conclusions

The high quality spectra easily obtained from emeralds with the Nicolet 6700 FT-IR spectrometer can provide valuable information to aid in verifying that a sample is an untreated natural emerald. In the case of synthetic emeralds, the spectra from the flux process have very low water levels and weak peaks in the hydroxyl region. In many stones created by the hydrothermal process, peaks corresponding to the presence of ammonium ions and chloride species can be used for identification purposes. However, emeralds created by the Russian hydrothermal process have spectra very similar to natural stones and a definitive identification is difficult. In the case of treated stones, the C-H stretch region around 3000 $cm^{-1}$ clearly reveals the presence of organic material. If the peaks are small and correspond to aliphatic hydrocarbons, they may be due to oil from the skin or a natural oil rubbed into the surface. If the peaks are stronger and correspond to aromatic hydrocarbon, it is likely that the stone has been treated. While no analytical technique can solve every problem, FT-IR spectroscopy plays a valuable role in modern gemological laboratories. Creating workflows with Thermo Scientific TQ Analyst™ and Thermo Scientific OMNIC™ macros can provide push-button analysis for many key analyses.

## References

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