

THE SEPARATION OF NATURAL FROM SYNTHETIC EMERALDS BY INFRARED SPECTROSCOPY

By Carol M. Stockton

Infrared spectroscopy provides a means to distinguish natural from synthetic emeralds in the range 2000–5000 cm^{-1} , as determined by a study of spectra obtained from 37 natural, 19 hydrothermal synthetic, and 38 flux synthetic emeralds from a variety of sources. The technique is nondestructive and, with Fourier transform instrumentation, extremely rapid in comparison to most laboratory methods. It is especially useful for identifying stones that contain no distinguishing inclusions.

Various manufacturers continue to produce and introduce synthetic emeralds (figure 1). Although inclusions usually enable gemologists to distinguish natural from synthetic emeralds, flawless stones may be extremely difficult to identify by conventional gemological means. Laboratory methods (e.g., microprobe, X-ray fluorescence) that involve equipment that is generally too expensive for practical ownership by most gemologists can then be applied as a last resort. More than one of these has proved useful in separating synthetic from natural emeralds (Griffiths and Nassau, 1980; Kuhlmann, 1983; Schrader, 1983; Troup and Hutton, 1983; Stockton, 1984), but the methods are generally time-consuming. By contrast, Fourier transform infrared (FTIR) spectrometry, especially when accompanied by an automated micro-beam chamber, provides rapid, completely non-destructive results in less than five minutes (Fritsch and Stockton, 1987).

MATERIALS AND METHODS

It was thus relatively simple to obtain the infrared spectra of 37 natural and 57 synthetic (19 hydrothermal and 38 flux) emeralds, most of which are from the GIA reference collection. The natural emeralds came from a variety of localities: all those reported in Stockton (1984) as well as specimens recently acquired from Afghanistan, Pakistan, and new localities in northern Brazil and southern Tanzania (see table 1). The synthetics also include those in the previous study and samples from Russia (both flux and hydrothermal),

Swarovski in Austria and Ustan in the U.S. (both noncommercial), and Lennix (France).

Unpolarized spectra were acquired in the range 400–5000 cm^{-1} with a Nicolet 60SX FTIR spectrometer. However, complete absorption occurs below about 2200 cm^{-1} , so the spectra reported here are shown only for the range 2000–5000 cm^{-1} .

THE SEPARATION OF NATURAL FROM SYNTHETIC EMERALDS

As can be seen in figure 2, flux synthetic emeralds can readily be distinguished from their natural and hydrothermal synthetic counterparts. The most obvious difference is the absence in the flux stones of the strong absorption between 3400 and 4000 cm^{-1} . This strong absorption has been identified as being associated with water (Wood and Nassau,

TABLE 1. Origin and number of samples of natural and synthetic emeralds tested by Fourier transform infrared spectroscopy.

Origin	No. of samples
Natural	
Afghanistan	1
Brazil	12
Colombia	17
Norway	1
Peru	1
Sandawana	2
South Africa	1
Tanzania	1
USSR	1
Flux-grown synthetic	
Chatham	7
Gilson	5
Inamori	2
Lennix	2
USSR	4
Ustan	3
Unknown	15
Hydrothermal synthetic	
Biron	5
Linde	2
Regency	2
Swarovski	1
USSR	3
Unknown	6

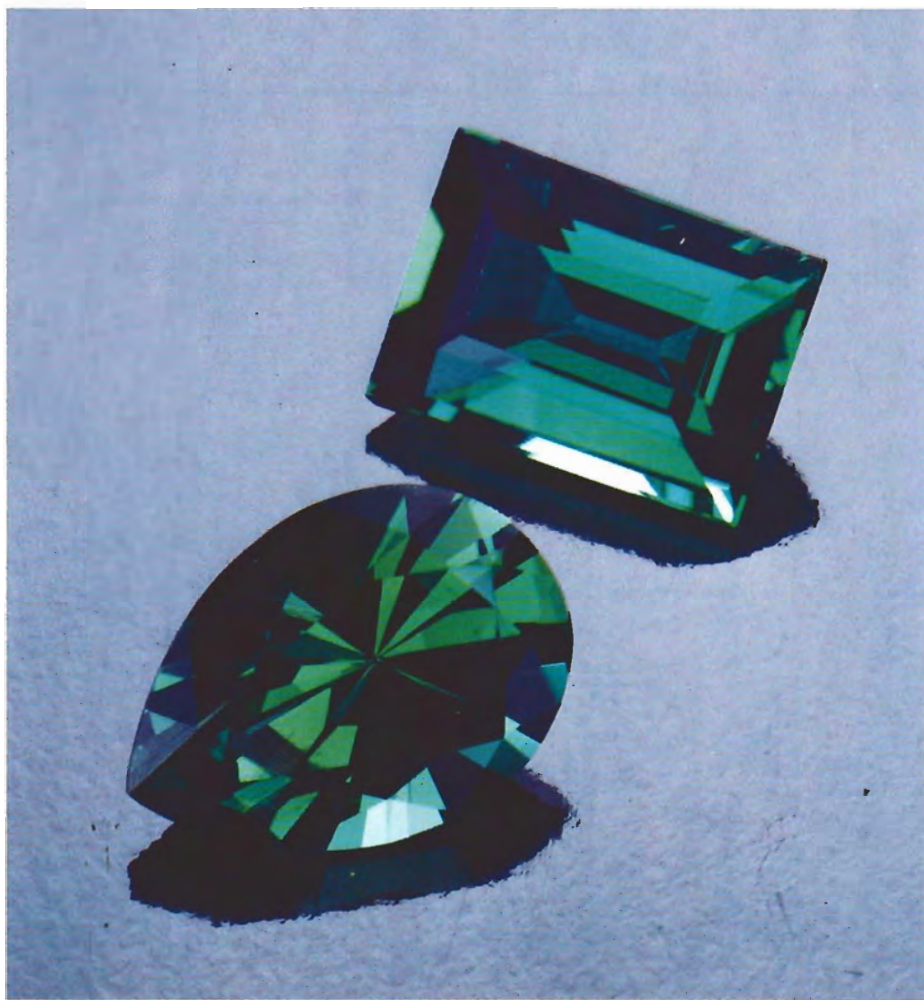


Figure 1. Among the more recent synthetic emeralds introduced are the Biron hydrothermal (top, 0.54 ct) and the Inamori flux (bottom, 0.56 ct) products. Photo © Tino Hammid.

1968], which is always present in natural and hydrothermal synthetic emeralds because of their growth conditions.

The infrared spectra of natural and hydrothermal synthetic emeralds are more similar to one another. However, all but two types of hydrothermal synthetics exhibit a pattern of strong absorption features between 2600 and 3000 cm^{-1} that readily distinguishes them from their natural counterparts (figure 2). Most of the absorption features seen in this range for synthetics were also seen to some degree in natural emeralds, but never all together in the magnitude and same relative strengths as in the synthetics. Moreover, some features that were observed in most hydrothermal synthetics—for example, those at about 2745 , 2830 , 2995 , 3490 , 4052 , and 4375 cm^{-1} —were never detected in natural emeralds. Thus, the overwhelming majority of hydrothermal synthetic emeralds can be distinguished from natural emeralds by infrared features in this region. No

interpretation of these features has been published, and it is not within the scope of this study to determine their causes, but it is hoped that future researchers will do so.

As mentioned above, two types of hydrothermal synthetic emeralds presented greater difficulty in identification. One is a product that was grown experimentally between 1961 and 1974 by Dr. R. Haupt at Swarovski in Austria, but was never commercially released (K. Schmetzer, pers. comm. to R. Kane, 1987); one sample of this product was included in the study. The other is the Russian hydrothermal product, which is now available commercially and is, therefore, of greater

ABOUT THE AUTHOR

Ms. Stockton is senior research gemologist in the Research Department of the Gemological Institute of America, Santa Monica, California.

© 1987 Gemological Institute of America

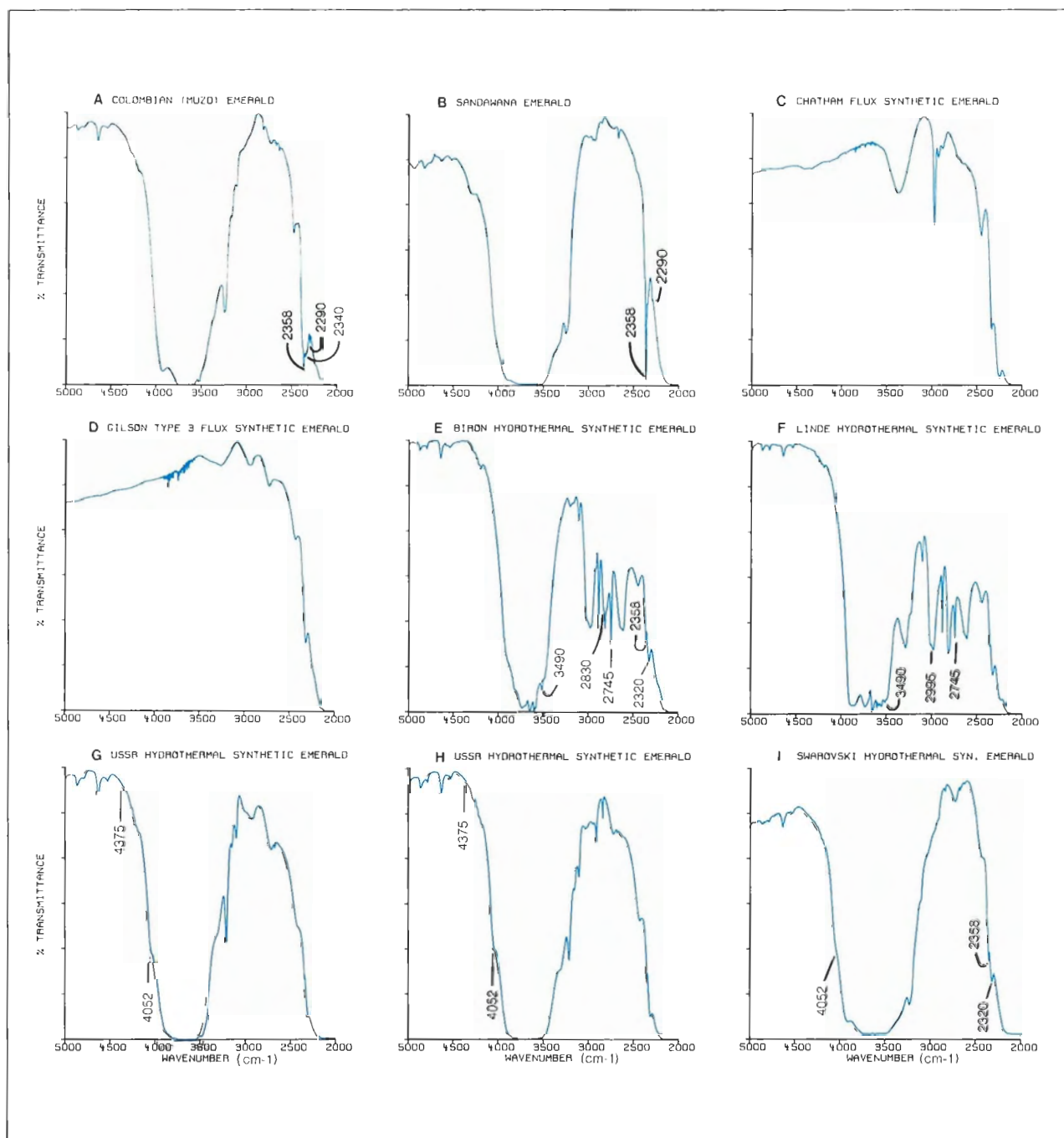


Figure 2. A representative sample of infrared spectra for two natural emeralds (a and b), two flux-grown synthetic emeralds (c and d), two hydrothermal synthetic emeralds (e and f), two Russian hydrothermal synthetic emeralds (g and h), and a Swarovski hydrothermal synthetic emerald (i). Features that can be used to distinguish natural emeralds from hydrothermal synthetics are labeled on spectra a and b. The flux synthetic emerald spectra c and d clearly lack the strong absorption at about $3400\text{--}4000\text{ cm}^{-1}$ that is evident in the spectra of all the natural and hydrothermal synthetic emeralds. The spectra of hydrothermal synthetic emeralds (e–i) illustrated here also exhibit features (labeled) that can be used to distinguish these synthetics from natural emeralds. The Russian and Swarovski synthetics (g, h, and i) are most similar to natural emeralds; although the diagnostic spectral features (labeled) are relatively small, they are still distinctive.

concern; three samples of this material were studied. All four of these specimens showed spectra that are deceptively similar to those of natural emeralds (figure 2). Fortunately, a close inspection revealed features that, while not obvious, are nevertheless distinctive. All three Russian stones have two of the features mentioned above, at 4052 and 4375 cm^{-1} , that were not observed in any of the specimens of natural emerald, but can be detected in most hydrothermal synthetics. In the Swarovski specimen, the 4052 cm^{-1} feature occurs, although weakly, while the 4375 cm^{-1} band could not be observed.

Features in the 2200–2400 cm^{-1} range can also be used to distinguish these troublesome hydrothermals from natural emeralds. The latter show at least two and, more commonly, three features in this region, at about 2290, 2340, and 2358 cm^{-1} . The 2290 cm^{-1} band was never observed in the synthetics, while it is usually present (in all but two of the 37 samples here) in natural emeralds. In the synthetics, the location of the "2340" band ranges from 2310 to 2329 cm^{-1} , while in natural stones it is located between 2335 and 2342 cm^{-1} , a distinction that can be made easily with a good infrared spectrometer. Moreover, in natural emeralds the 2358 cm^{-1} band,

associated with structural CO_2 (Wood and Nassau, 1968), is always stronger than the 2340 cm^{-1} feature, while in synthetics the relationship is reversed.

DISCUSSION

It should be remembered that emeralds, both natural and synthetic, are doubly refractive. As a result, their infrared spectra are affected by the orientation of the sample to the incident beam of energy. Ideally, spectra should be taken at known crystallographic orientations in order to control for these variations, but cut gemstones rarely lend themselves to such conditions. While none of the diagnostic features completely disappeared at any orientation tested, some did become quite weak and a less sensitive instrument could fail to detect the relevant features in some cases. It is, therefore, important that spectra be obtained at two or three different orientations before any conclusion is drawn as to the origins of a particular sample.

The results of this study suggest that infrared spectroscopy provides additional means to distinguish natural from synthetic emeralds. With a Fourier transform instrument, the analysis is rapid as well as nondestructive and can frequently be done even on mounted emeralds.

REFERENCES

- Fritsch E., Stockton C.M. (1987) Infrared spectroscopy in gem identification. *Gems & Gemology*, Vol. 23, No. 1, pp. 18–26.
- Griffiths J.E., Nassau K. (1980) Raman spectra of light-coupling prism and gemstone materials. *Applied Spectroscopy*, Vol. 34, No. 4, pp. 395–399.
- Kuhlmann H. (1983) Emissionsspektralanalyse von natürlichen und synthetischen Rubinen, Saphiren, Smaragden und Alexandriten. *Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 32, No. 4, pp. 174–195.
- Schrader H.-W. (1983) Contributions to the study of the distinction of natural and synthetic emeralds. *Journal of Gemmology*, Vol. 15, No. 8, pp. 422–434.
- Stockton C.M. (1984) The chemical distinction of natural from synthetic emeralds. *Gems & Gemology*, Vol. 20, No. 3, pp. 141–145.
- Troup G.J., Hutton D.R. (1983) The use of electron spin resonance spectroscopy to distinguish synthetic from natural gemstones. *Journal of Gemmology*, Vol. 18, No. 5, pp. 421–431.
- Wood D.L., Nassau K. (1968) The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *American Mineralogist*, Vol. 53, No. 56, pp. 777–800.