
INFRARED SPECTROSCOPY IN GEM IDENTIFICATION

By Emmanuel Fritsch and Carol M. Stockton

Infrared spectroscopy is a powerful tool for gem identification and research. Absorptions of a gem material in the infrared region of the electromagnetic spectrum are due to vibrations in the crystal structure; they can be used to help separate one gem material from another or to detect certain types of treatments. The authors describe the new Nicolet 60SX Fourier transform infrared spectrometer recently acquired by GIA's Research Department, and outline the detection of polymer-impregnation of opal as an example of the use of infrared spectroscopy in gemology.

Infrared spectroscopy in itself is not new, having become generally available to scientists about 50 years ago. However, technological advances in instrumentation in the past 10 years have made infrared spectra much more readily and rapidly accessible. In recent years, this spectroscopy has been used in several instances by a number of gemologists (e.g., Arnould and Poirot, 1975; Zecchini, 1979); and since its arrival at the GIA Research Department in January 1986, the Nicolet 60SX Fourier transform infrared (FTIR) spectrometer (see box) has consistently proved its value in gemological applications. As a result, gemologists can expect to encounter numerous reports in the future that involve the use of infrared spectroscopy. This article is intended to introduce gemologists to the concepts, instrumentation, and terminology of infrared spectroscopy, as well as to illustrate the usefulness of this technique through several examples, in particular the distinction of natural from polymer-impregnated opals (figure 1).

INFRARED ENERGY

The infrared region of the electromagnetic spectrum is the energy range just beyond the red end of the visible spectrum. In fact, the term *infrared* is derived from being lower in energy ("infra-") than the red end. The unit by which infrared energy is usually measured is the wavenumber (number of waves per centimeter), which is expressed in reciprocal centimeters (cm^{-1}). The infrared is thus referred to as the energy range between $13,333 \text{ cm}^{-1}$ (the edge of the red) and 33 cm^{-1} (a limit determined by use and technology). Alternatively, infrared radiation can be expressed in wavelength units, traditionally the micrometer ($1 \mu\text{m} = 1,000 \text{ nm} = 10,000 \text{ \AA}$), or in another energy unit, electron volts (eV). This broad region is divided on the basis of experimental techniques and applications into three parts: near infrared, mid-infrared, and far infrared (figure 2). For most gemological purposes, infrared energy is

ABOUT THE AUTHORS

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

Acknowledgments: The authors wish to thank Dr. George Rossman, of the California Institute of Technology (CalTech), who recommended the application of infrared spectroscopy to the detection of impregnated opals and provided access to CalTech's FTIR spectrometer before GIA acquired its own system.

© 1987 Gemological Institute of America



Figure 1. One of these two opals (7.00 and 1.14 ct) has been treated with polymer to improve its play of color, while the other is completely natural. No traditional gemological tests can distinguish between the two and, until now, laboratory testing took hours. With the infrared techniques described in this article, however, identification can be done in a matter of minutes (see figures 6 and 8). Photo © Tino Hammid.

expressed in cm^{-1} ; energies above 400 cm^{-1} —that is, the mid-infrared and the near infrared—are of greatest interest gemologically.

APPLICATIONS OF INFRARED SPECTROSCOPY

Absorption features in the visible range are largely due to electron transitions, including those that generate color, such as occur with chromium atoms in the corundum lattice and cause the color of rubies. In the infrared, however, spectral features generally arise from vibrations (as well as, in the far infrared, from rotations) of molecular and structural components of the crystal. For example, carbon in diamond and water when present in a gemstone have characteristic signals in the infrared.

Crystal structures consist of atoms held together by chemical bonds. A possible analogy to describe these bonds is to think of them as springs connecting heavy weights such that the weights representing atoms have the ability to vibrate. Every group of atoms has a number of intrinsic vibration frequencies that correspond to rocking, stretching, or bending of the bonds between the atoms of the group (see figure 3). In order to actually vibrate, the structure must extract energy from some source, in this case a beam of incident infrared radiation, giving rise to an absorption band. This band is usually very sharp for organic

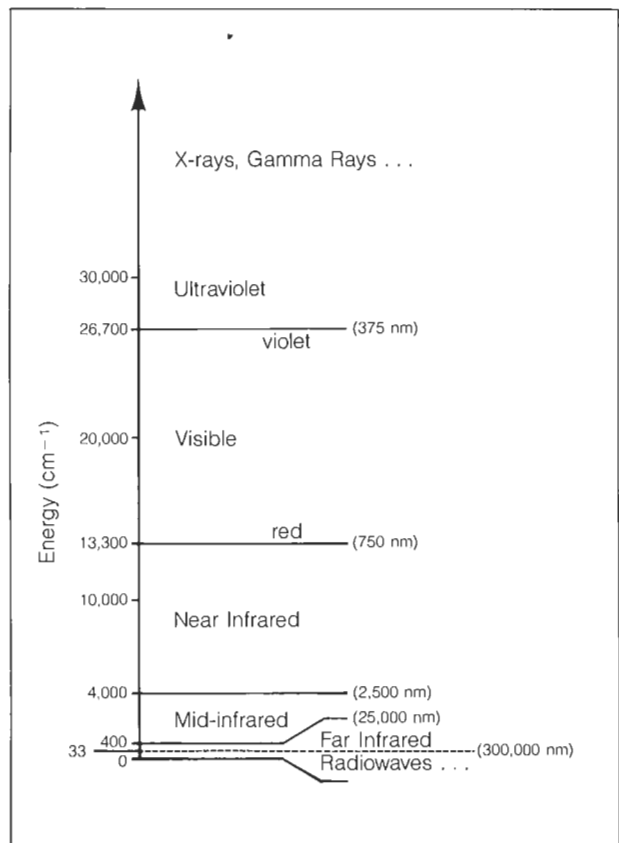


Figure 2. The position of the infrared region and its three subdivisions in the electromagnetic spectrum.

THE NICOLET 60SX FOURIER TRANSFORM INFRARED SPECTROMETER



Figure 1A. The Nicolet 60SX FTIR spectrometer. Photo courtesy of Nicolet Instrument Corp.

This spectrometer (figure 1A) is a state-of-the-art instrument capable of measuring spectra between 400 and 25,000 cm^{-1} —that is, through the entire mid- and near infrared, as well as visible, ranges.

How an Infrared Spectrometer Works. In a typical dispersive instrument, the beam is split into two parts: One goes through the sample, while the other passes through a reference. Each beam is dispersed through a prism or a grating, and the absorption at one particular wavelength is analyzed by partially ob-

structing the reference beam, until the same amount of energy goes through both beams. An FTIR spectrometer contains two parts that do not exist in classical dispersive instruments: a Michelson interferometer, which combines all the incoming infrared radiation into one "interferogram," and a mathematical program that operates on the principle of the Fourier transform, which converts an interferogram back into a spectrum. In the FTIR concept, the light is split into two halves by a semitransparent mirror (called a beamsplitter). These two beams are then

reflected back toward one another by two additional mirrors, one fixed, the other moving, so that the two beams "interfere" when they come back together at the beamsplitter, giving rise to an interferogram.

Figure 1B shows the optical path of the infrared radiation in a classical dispersive spectrometer, compared with the way the same radiation is handled through an FTIR instrument. In the Fourier transform instrument, when the moving mirror is at exactly the same distance from the beamsplitter as the fixed mirror (or the same distance plus an integer times half the wavelength), the interference is constructive (i.e., the two intensities are added together). Otherwise, the interference is destructive. With such a configuration, the further the moving mirror travels, the better two very close frequencies will be separated. In this manner, a very good resolution is obtained without cutting down the amount of energy, a problem inherent to any dispersive instrument. The interferogram then goes through the sample, and parts of the wavelengths are absorbed. The transmitted wavelengths—still in the form of an interferogram—reach the detector. The data are digitized and processed using a Fourier transform program, which (through a sequence of many steps) basically transforms the final interferogram into a transmission spectrum and eventually into an absorption spectrum.

The FTIR spectrometer has a number of important advantages over the older dispersive instrument. Because the entire spectrum is recorded at the same time in the form of an interferogram, there is no need to mechanically scan one wavelength after the other. Thus, where 20 minutes were needed in the past to obtain a spectrum using a dispersive instrument, only a fraction of a second is required on an FTIR spectrometer. This allows the operator to run 100 or even 1,000 spectra of the same sample in a very short time and then average the results in order to reduce the random "noise" and bring out weak bands that often contain essential information. There is also reduced heating of the sample, in contrast with dispersive instruments, and the consequent spectral perturbations are largely avoided.

In addition, the FTIR concept uses a laser both to check the moving mirror displacements and as an internal reference for wavelength, another feature that is not found on the dispersive spectrometer.

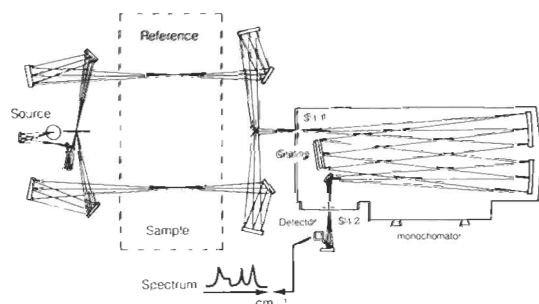
A further advantage is that the Nicolet 60SX spectrometer is monitored by a powerful computer that not only does the mathematics of the Fourier transform, but also provides considerable flexibility to plot, display, store, and manipulate spectra. Basically, then, an FTIR spectrometer is both faster and more accurate than a dispersive instrument.

How Spectra Are Obtained from Gemstones. A transparent gemstone is usually cut in such a way that light returns to the eye, creating the brilliance and fire of the gem. The problem in spectroscopy is exactly the reverse: How do we get light to pass through the stone and emerge on the other side? Several sample holder "attachments" are available on an FTIR spectrometer to achieve this purpose.

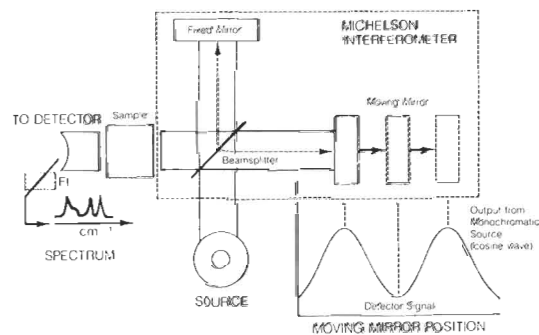
The most useful adapter is probably the micro-beam chamber, where a curved mirror focuses the beam down to an area the size of a pinhead, or smaller. This intense, focused beam can then be passed with relative ease through a very tiny culet or the girdle of a stone to obtain a spectrum.

For nontransparent materials, such as jade and turquoise, the diffuse reflectance attachment provides satisfactory spectra, with the beam of energy barely penetrating the surface of the sample, "bouncing" off, and then being collected by a curved mirror before passing to the detector.

Figure 1B. Comparison of the principle of a dispersive infrared spectrometer with that of an FTIR instrument. The monochromator in the former is replaced by an interferometer and Fourier transform program in the latter (after Nicolet User's Manual, 1986).



Typical Dispersive Spectrometer Design



FTIR System Concept

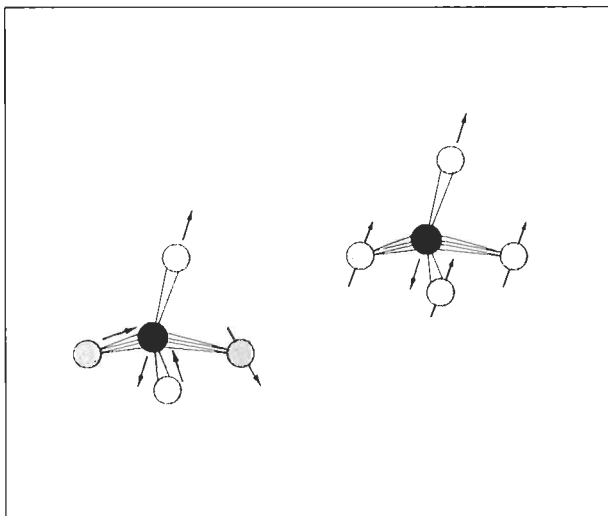


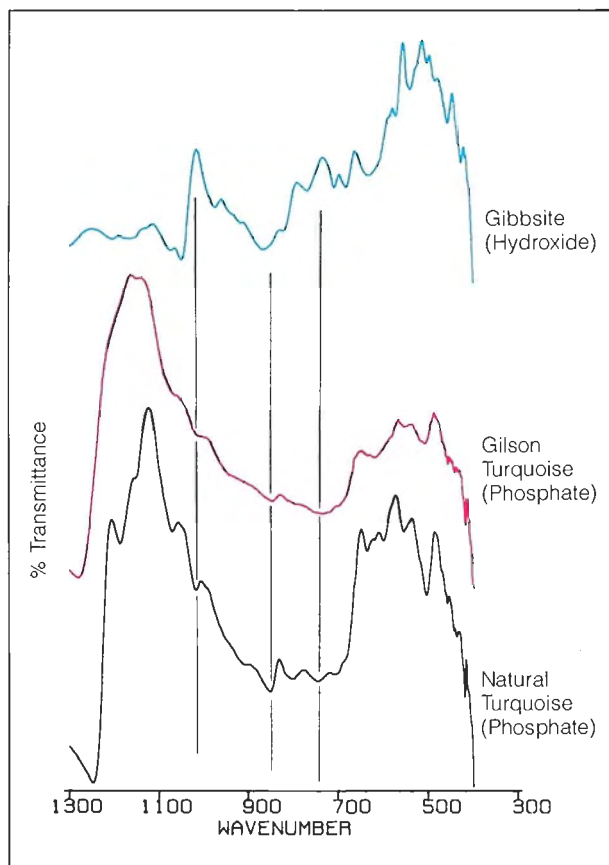
Figure 3. The vibrations of atoms in, for instance, a tetrahedral unit—such as in the SiO_4 tetrahedron of silicates and quartz illustrated here—are responsible for the absorption of infrared radiation (after Conley, 1972).

molecules (such as polyester), and infrared spectroscopy has, indeed, been most extensively developed for organic chemistry.

Gemstone Identification through Characteristic Infrared Spectra. Inorganic materials, including gemstones, also have characteristic vibrational energies in the infrared that can be used for identification. However, their spectral features are usually broader than for organic molecules. An analogy can be made with X-ray diffraction, where a pattern for a given mineral is the “fingerprint” of its atomic structure. For infrared spectroscopy, absorptions associated with the vibrations of the crystal structure (“lattice vibrations”) are characteristic of the given combination of atoms constituting the gemstone. A good example is provided by turquoise: Natural turquoise—a phosphate, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 5\text{H}_2\text{O}$ —can be distinguished easily from one of its common substitutes, gibbsite—a hydroxide, $\text{Al}(\text{OH})_3$ —by features in the mid-infrared. Because the two materials are so different chemically, their patterns are also very different (see figure 4). Even Gilson turquoise, which is a synthetic, exhibits a significantly smoother pattern when compared with natural turquoise, because of a different state of aggregation (Arnould and Poirot, 1975; Rossman, 1981).

Detection of “Water” and Its Significance in Gemology. “Water,” either molecular (H_2O) or as hydroxyl groups (OH) is combined in various forms in many gemstones or is present as an impurity. These various forms of water have characteristic patterns in the mid-infrared and can be good indicators of structure, origin, or treatment. Preliminary results show that natural amethyst can be distinguished from its synthetic analog on the basis of slightly different types of water absorptions. Water is typically the first component to leave a mineral on heating; therefore, there is some hope that infrared spectroscopy may also be useful in identifying the absence of heat treatment in some water-containing gemstones (Aines and Rossman, 1985).

Figure 4. Gem identification with infrared spectra: Natural turquoise has a very different spectrum compared to that of gibbsite, an increasingly common substitute. Gilson man-made turquoise exhibits flattened features. For the purpose of this illustration, transmittance values are arbitrary.



Detection of Gemstone Impregnation. The extensive documentation by organic chemists of the characteristic infrared absorption spectra of organic compounds is very helpful in recognizing impregnation in gemstones. One or more sharp bands will show up in the spectrum of an impregnated stone that are not present in the spectra of similar untreated stones. A detailed example of how this is applied to impregnated opal appears below. Not only does infrared spectroscopy enable one to detect impregnation, but the additional bands can also reveal which species of polymer or other material has been used to process the stone.

Other Applications. Infrared spectroscopy reveals characteristic patterns for different types of diamonds (Ia, Ib, IIa, IIb), inasmuch as both nitrogen and boron impurities trapped in the diamond lattice have absorption features in the mid-infrared. One of the most significant gemological uses recently revealed for the near infrared is detection of the H1b and H1c bands (4941 and 5165 cm^{-1} , respectively), which identify that a diamond has been irradiated and heat treated to produce or enhance yellow to brown coloration (Woods, 1984; Woods and Collins, 1986).

THE DETECTION OF POLYMER-IMPREGNATION OF OPAL BY MEANS OF FTIR SPECTROSCOPY

The ability of infrared spectroscopy to provide information about various organics, plastics, dyes, and hydroxides makes this technique particularly useful in the study of opal, especially the detection of treatment. Until now, the only positive method of identifying polymer-impregnation of opals (including impregnation with plastics and, more recently, with silicon-based polymers) has been examination with an electron microscope (Manson, 1978), a time-consuming and expensive procedure.

The infrared spectra of opals in the 4000–9000 cm^{-1} range have been well characterized (e.g., Langer and Flörke, 1974). While the spectra of natural opals vary somewhat, all exhibit a broad transmission region between 5300 and 6800 cm^{-1} and another between 4000 and 5000 cm^{-1} . The strongest absorption features lie between 5000–5300 cm^{-1} and 6700–7200 cm^{-1} , and have been attributed to combination vibrations of molecular water (H_2O). Weaker absorptions also usually occur at about 4400 and 4500 cm^{-1} , both caused by

vibrations of SiOH groups, as well as at 5500 cm^{-1} (figure 5).

We examined 15 natural, untreated opals by FTIR spectroscopy and found that all displayed infrared spectra consistent with the above general pattern. These samples (figure 6) include Australian white, gray, and black opal; Brazilian white and hydrophane opal; and (from various localities) blue, brown, orange, and transparent colorless opal with play of color, red-orange and yellow non-phenomenal transparent opal, and green chrysopal ("prase opal"). Variations among their spectral features (figure 7) are related to differences in microstructure, hydroxyl content, and organic impurities.

We also examined 23 polymer-impregnated opals by FTIR spectroscopy (figure 8). They include opals treated as long as 10 years ago as well as stones treated within the last two years; some of these can be detected by electron microscopy and some cannot. White, black, brown, blue, and orange background colors are represented.

Without exception, the impregnated opals exhibit absorption features in the infrared that have

Figure 5. The near-infrared spectrum of a natural, untreated white opal from Australia. Absorption features characteristic of opal are labeled.

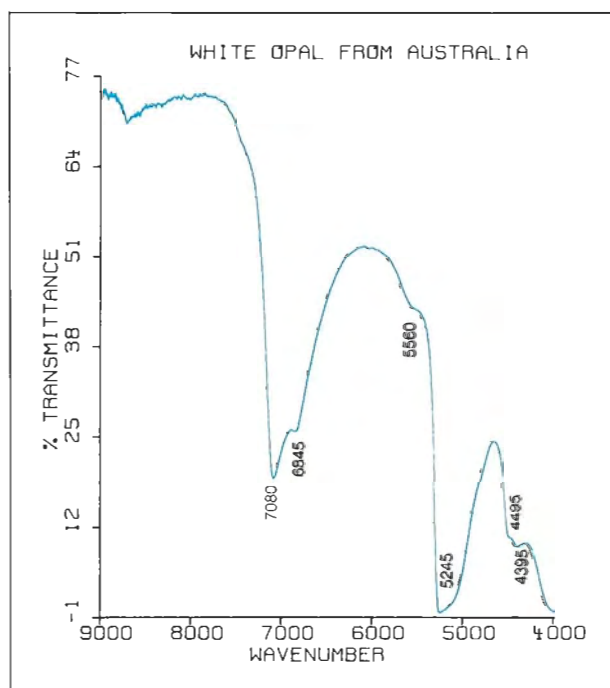
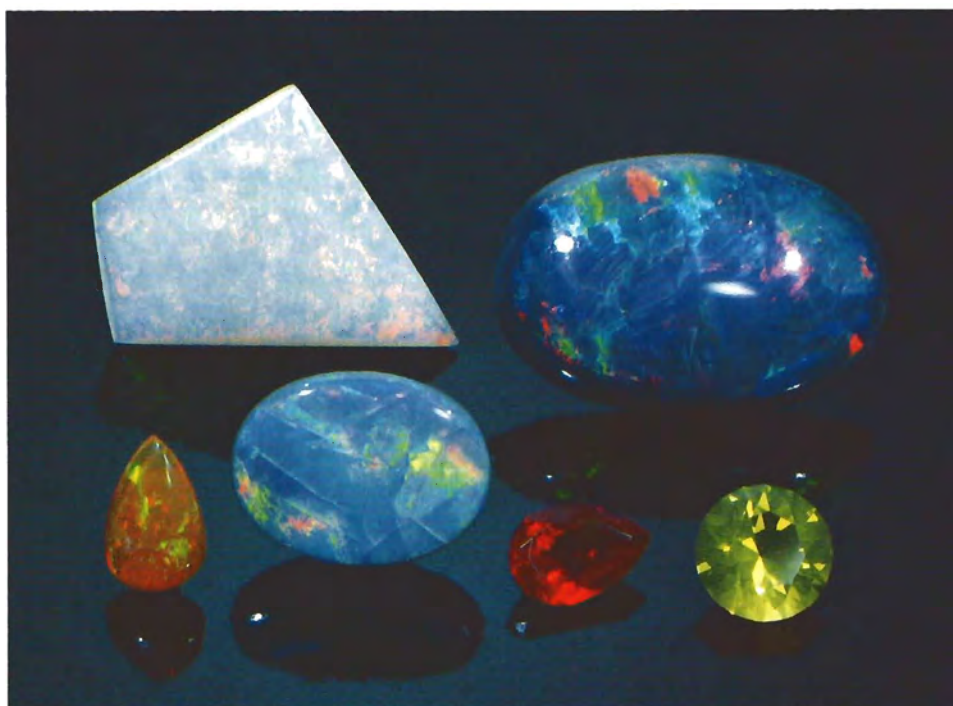


Figure 6. Several of the natural, untreated opals (0.88–14.79 ct) examined for this study, including material from Australia, Brazil, Mexico, and Idaho. Photo © Tino Hammid.



never been reported for *any* natural, untreated opals. Two types of spectra can generally be distinguished for these treated opals. The first has strong overlapping features at about 5725 and 5810 cm^{-1} , with weaker bands at about 4265, 4350, 4670, and 4775 cm^{-1} (figure 9). The second has strong overlapping bands at 5780, 5890, and 5925 cm^{-1} ; distinct features at 4735 and 6155 cm^{-1} ; and lesser ones at 4270, 4350, and 4405 cm^{-1} (figure 10).

Because of the overlap of features in the 4300–4500 cm^{-1} range found in both treated and untreated specimens, however, we do not recommend the use of bands in this region to determine treatment.

The exact cause of each feature has not yet been identified; nor has correlation been made with the types of materials being used for impregnation. However, consistent differences in the spectra of impregnated as compared to untreated

Figure 7. Near-infrared spectra of the Australian black, Idaho yellow, and Mexican red-orange opals pictured in figure 6. In spite of the variability exhibited among these spectra, their basic similarity to the spectrum in figure 5 is evident.

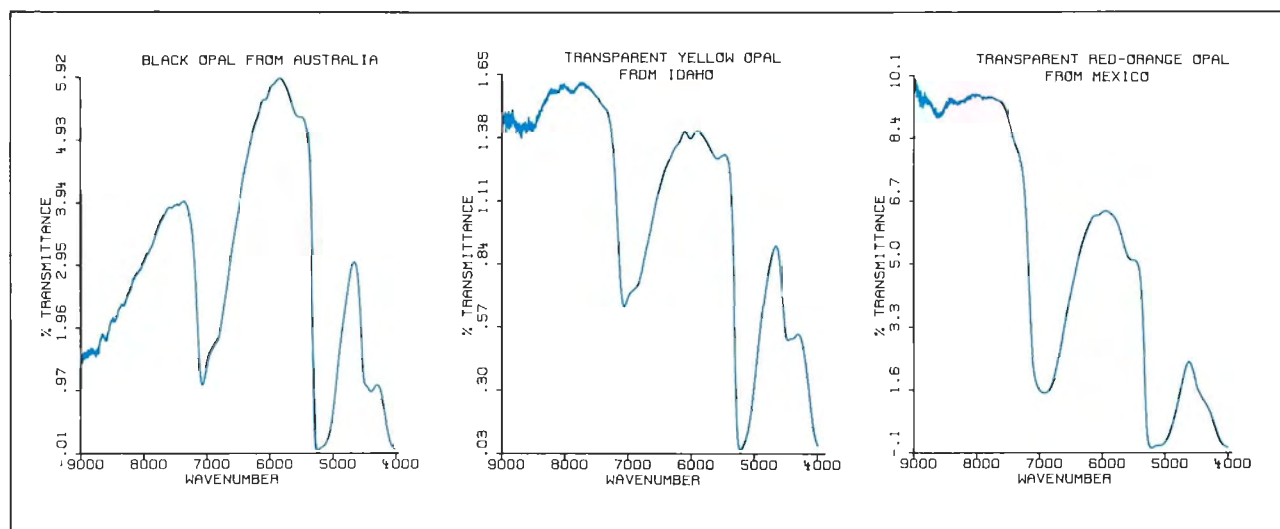




Figure 8. A representative sample (1.00–20.37 ct) of the polymer-impregnated opals examined for this study. Some of these can also be detected by electron microscopy, while others cannot.

Photo © Tino Hammid.

opals are sufficient to deduce that certain features are related to the impregnation materials. Thus, a new method for the identification of polymer-impregnated opal, faster and more foolproof than the old electron microscope test, has been identified. It should be noted, as a caution, that identification of treated opals by infrared spectroscopy applies only to opals treated with polymer-type materials. Sugar- and smoke-treated opals exhibit no significant differences from untreated opals in the 4000–9000 cm^{-1} region. Identification of these older types of treatment rests in the use of the gemological microscope (e.g., Gübelin, 1964).

CONCLUSION

Infrared spectroscopy has now joined the ranks of laboratory techniques that can be applied to solv-

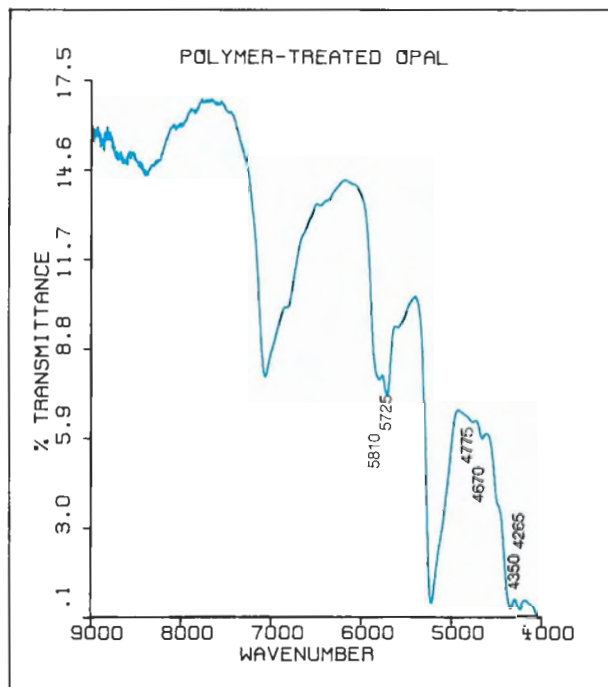
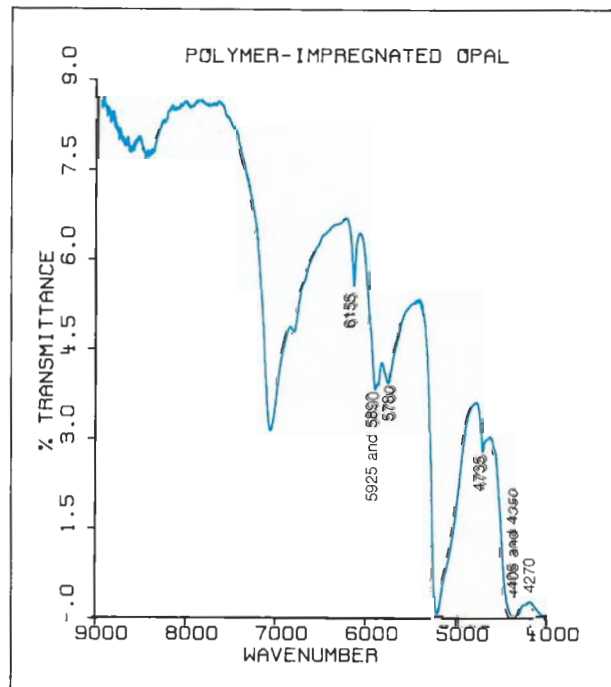


Figure 9. The near-infrared spectrum of the opal at top left in figure 8 is representative of the first type described for polymer-treated opals in the text. Absorption features diagnostic of the treatment are labeled.

Figure 10. The near-infrared spectrum of the opal at middle right in figure 8 is representative of the second type described in the text. Absorption features diagnostic of the treatment are labeled.



ing gemological problems that have thus far eluded solution by traditional gem-testing techniques. Reports on the use of infrared spectroscopy by other scientists to identify irradiation and annealing of diamonds (Woods, 1984; Woods and Collins, 1986) as well as treatment and synthesis of other gem materials (Langer and Abu-Eid, 1977; Zecchini, 1979; Dontenville et al., 1986) indicate that infrared analysis is gaining popularity for gemological applications.

Other projects using infrared spectroscopy that are now under way in the GIA Research Department include:

- Colored diamonds, especially the presence of treatment-related absorptions in the near infrared
- Natural/synthetic separations: amethyst and corundum
- Impregnation: identification of the presence of organic polymers in gemstones other than opal, such as turquoise

- Gem identification through fundamental lattice vibrations: turquoise vs. gibbsite, jadeite vs. nephrite, etc.

To increase our knowledge of gemstones, and to simplify identification procedures by comparison with standard references, the GIA Research Department will also create a library of gemstone infrared spectra. Each spectrum will be correlated with the stone's geographic origin or method of synthesis, its chemistry, the orientation of the crystal, and standard gemological properties.

In the near future, the above applications will be developed and infrared spectroscopy will be extensively used to help detect other forms of treatment, especially heat treatment, inasmuch as water is usually one of the first components to be modified (Aines and Rossman, 1985). All these ongoing studies suggest that infrared spectroscopy is one of the most promising analytical techniques available today for resolving otherwise elusive gemological problems.

REFERENCES

- Aines R.D., Rossman G.R. (1985) The high temperature behavior of trace hydrous components in silicate minerals. *American Mineralogist*, Vol. 70, pp. 1169–1179.
- Arnould M., Poirot J.-P. (1975) Spectrographie infrarouge par reflexion de la turquoise et de quelques-uns de ses substitués. *Bulletin de l'Association Française de Gemmologie*, Vol. 44, pp. 9–10.
- Conley R.T. (1972) *Infrared Spectroscopy*, 2nd ed. Allyn and Bacon, Boston.
- Dontenville S., Calas G., Cervelle B. (1986) Etude spectroscopique des turquoises naturelles et traitées. *Revue de Gemmologie A.F.G.*, No. 85, pp. 8–10, and No. 86, pp. 3–4.
- Gübelin E.J. (1964) Black-treated opals. *Gems & Gemology*, Vol. 11, No. 5, pp. 157–159.
- Langer K., Abu-Eid R.M. (1977) Measurement of the polarized absorption spectra of synthetic transition metal-bearing silicate microcrystals in the spectral range 44,000–4,000 cm^{-1} . *Physics and Chemistry of Minerals*, Vol. 1, pp. 273–299.
- Langer K., Flörke O.W. (1974) Near-infrared absorption spectra (4000–9000 cm^{-1}) of opals and the role of "water" in these $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ minerals. *Fortschritt der Mineralogie*, Vol. 52, No. 1, pp. 17–51.
- Manson D.V. (1978) Plastic impregnated gem opal. *Gems & Gemology*, Vol. 16, No. 2, pp. 49–57.
- Rossman G. (1981) Color in gems: the new technologies. *Gems & Gemology*, Vol. 17, No. 2, pp. 60–72.
- Woods G.S. (1984) Infrared absorption studies of the annealing of irradiated diamonds. *Philosophical Magazine B*, Vol. 50, No. 6, pp. 673–688.
- Woods G.S., Collins A.T. (1986) New developments in spectroscopic methods for detecting artificially coloured diamonds. *Journal of Gemmology*, Vol. 20, No. 2, pp. 75–82.
- Zecchini P. (1979) Etude de l'absorption infrarouge de quartz d'origine naturelle ou de synthèse. *Revue de Gemmologie A.F.G.*, No. 60, pp. 14–18.