POLYMER-IMPREGNATED TURQUOISE

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A large "Persian" turquoise cabochon was impregnated with a material that was also present in cavities on its base. Raman spectroscopy identified the filler as a UV-hardened polymer. Although such polymers have been seen as fillers in other gems, especially emerald, this is the first time the GIA Laboratory has seen turquoise treated with this material.

Turquoise has a cryptocrystalline structure that is composed of very fine, randomly oriented groups of tightly stacked parallel growths of pseudo-rhombohedral crystals (see King, 2002), which contributes to the porous nature of the material. Turquoise is a relatively stable mineral, as evidenced by a necklace showing no sign of deterioration that was found on the skeleton of a Native American dated to 1350 AD (again, see King, 2002). However, because it is porous, turquoise is vulnerable to skin oils or dirt when used in jewelry, both of which can produce a change in color. It is well known that the appearance and durability of turquoise may be enhanced by plastic impregnation, in a process referred to in the trade as *stabilization.*

During the 2007 Tucson gem show, these contributors encountered a 19.08 ct cabochon represented as Persian turquoise (figure 1). Although no treatments were disclosed, the sample had several small cavities and one large one in its base that were filled or partially filled with a transparent material (figure 1, right). Since this sample offered an excellent opportunity to characterize the material used for stabilization, we purchased it to conduct further studies in the laboratory. We collected standard gemological properties, as well as Raman spectra (using a Renishaw inVia Raman microspectrometer with a 514 nm laser at room temperature) and infrared spectra (using a Nicolet 6700 FTIR spectrometer equipped with a DRIFT accessory).

Results and Discussion. The spot RI was 1.60, and the SG (measured hydrostatically) was 2.48; the presence of the filler may be responsible for the relatively low SG value. With the desk-model spectroscope, the turquoise showed a 430 nm band (of moderate strength, due to iron absorption) and a weaker "smudge" at 460 nm. The turquoise was inert to long- and short-wave UV radiation, although the cavity edges fluoresced yellow to short-wave UV. There was no indication of dye when the sample was exposed to a thermal reaction tester (the color of any dye would be expected to bleed as the sample "sweated" next to the hot point). However, the transparent filler in the large cavity on the base of the cabochon emitted an acrid odor when tested with the hot point.

The characteristic bands in the Raman spectrum of the filler exposed on the base matched those of Norland

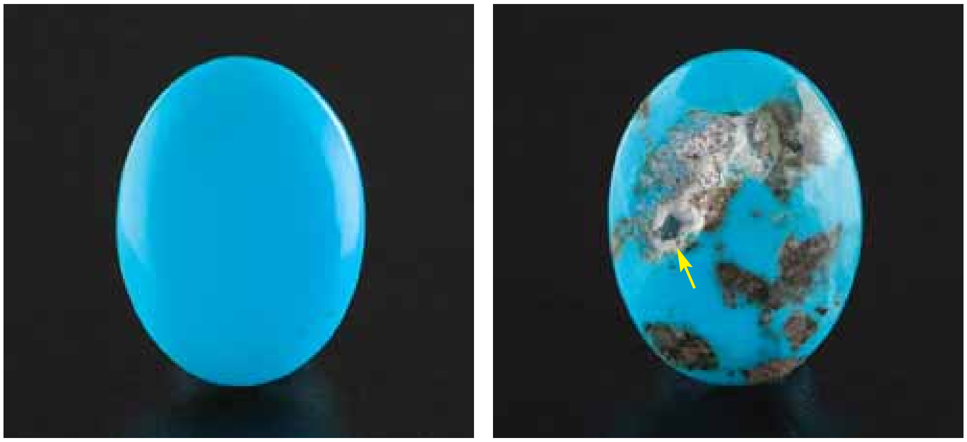


Figure 1. This 19.08 ct turquoise cabochon (top view on the left) was represented as "Persian," with no treatment disclosed. A large cavity visible on the base (right) is partially filled with a clear polymer, and a whitish residue can be seen in the rest of the cavity. The arrow points to a small transparent lump of the polymer, through which the blue color of the turquoise can be seen.

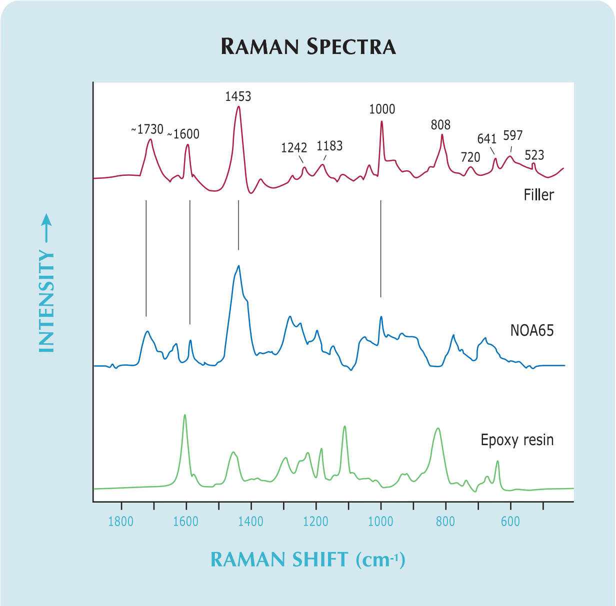


Figure 2. The Raman spectrum of the filling material exposed on the base of the turquoise cabochon shows bands that are characteristic of Norland Optical Adhesive 65. Some additional Raman bands (i.e., at 1242, 1183, 808, 720, 641, 597, and 523 cm^{-1}) suggest that this photopolymer may have been plasticized with other polymers. The Raman spectrum of epoxy resin, which is commonly used for gemstone impregnation, is shown for comparison.

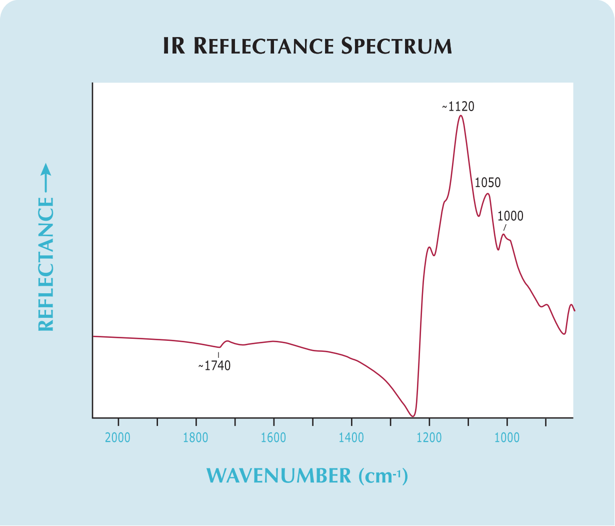
Optical Adhesive 65 (NOA 65, figure 2). This spectrum is quite different from that of the polymers typically used for gemstone filling/impregnation in the trade (e.g., for emerald and jade), such as epoxy resin. Bands characteristic of NOA 65 were observed at ~1730 (C=O stretching), ~1600, 1453 (CH$_3$-bending), and 1000 cm^{-1} (styrene phenyl ring; see Clarke et al., 1999; Miliani et al., 2002). In addition, strong bands in the 3100–2800 cm^{-1} region (not shown in the figure) are due to C-H stretching, and their intensity is related to the alkyl group (see Nørbygaard and Berg, 2004).

Raman spectroscopy of the top of the cabochon showed turquoise bands along with the major NOA 65 bands. This suggests that the NOA polymer was present throughout the stone, in addition to filling the cavities. Reflectance IR spectroscopy of the top of the cabochon (figure 3) showed turquoise peaks at ~1120, 1050, and 1000 cm^{-1}, as well as an absorption at ~1740 cm^{-1} that is the carbonyl band usually associated with polymers (see Learner, 1998; Fritsch et al., 1999). Since Raman spectroscopy eliminated the possibility of other types of polymers that can be identified by IR spectral features in the 2700–3300 cm^{-1} region, figure 3 focuses instead on the 2000–1000 cm^{-1} region, where distinctive bands due to plastics/polymers have been documented in impregnated turquoise.

NOAs are colorless liquid photopolymers. After curing with UV radiation, they become solid and thus polishable. The main advantages of NOAs for gem treatment are transparency, lack of color, and color stability; they can also provide mechanical stabilization of porous materials, such as turquoise, due to their high tensile strength. According to the company's web site (www.norlandprod.com), the NOA photopolymers are inert to sulfuric acid but exposure to acetone, dimethyl formamide, and ethylene dichloride will cause them to swell or soften (based on one-hour exposure time). NOAs are widely used in optical lamination (e.g., optical lenses, safety windows, holographic displays, and flat panel displays) as relatively thin films, 3 μm to ~1 mm. Although uncommon, such UV-hardened polymers have been used in the gem trade (e.g., Johnson et al., 1999; www.norlandprod.com/ApplicationsPageAdhesives.asp).

In addition to the Raman bands that are characteristic of NOA 65, we observed some minute extra Raman bands at 1242, 1183, 808, 720, 641, 597, and 523 cm^{-1}. Thus, we cannot eliminate the possibility of other NOA adhesives in the filler or plasticization with other polymers. Although we could not conclusively identify the filling material(s) in this turquoise, the characteristic Raman bands suggest that that it consists mainly of a UV-hardened polymer. IR absorption bands for plastic have been documented in impregnated turquoise at 1725 cm^{-1} (Lind et al., 1983), 1734 cm^{-1} (Dontenville et al., 1986), and at 1744 cm^{-1} (Pavese et

Figure 3. The reflectance IR spectrum of the cabochon in figure 1 reveals turquoise peaks at ~1120, 1050, and 1000 cm^{-1}. The absorption band at ~1740 cm^{-1} is caused by carbonyl, which is usually found in polymers.



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al., 2005). These studies and the present work (i.e., the IR absorption band at ~1740 cm^{-1}) suggest that various polymers/plastics have been used for stabilizing turquoise.

Conclusion. The use of a UV-hardened polymer for impregnating/filling a turquoise cabochon was documented using Raman and FTIR spectrometry. While such polymers have been previously used in gem trade (e.g., to fill emeralds), this is the first time we have seen them applied to turquoise.

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REFERENCES

Clarke R.H., Londhe S., Premasiri W.R., Womble M.E. (1999) Low-resolution Raman spectroscopy: Instrumentation and applications in chemical analysis. *Journal of Raman Spectroscopy*, Vol. 30, pp. 827–832.

Dontenville S., Calas G., Vervelle B. (1986) Étude spectroscopique des turquoises naturelles et traitées. *Revue de Gemmologie a.f.g.*, No. 85, pp. 8–10; No. 86, pp. 3–4.

Fritsch E., McClure S.F., Ostrooumov M., Andres Y., Moses T., Koivula J.I., Kammerling R.C. (1999) The identification of Zachery-treated turquoise. *Gems & Gemology*, Vol. 35, No. 1, pp. 4–16.

Johnson M.L., Elen S., Muhlmeister S. (1999) On the identification of various emerald filling substances. *Gems & Gemology*, Vol. 35, No. 2, pp. 82–107.

King R.J. (2002) Turquoise. *Geology Today*, Vol. 18, No. 3, pp. 110–114.

Learner T. (1998) The use of a diamond cell for the FTIR characterization of paints and varnishes available to twentieth century artists. *Postprints: IRUG*^{2}, Infrared and Raman Users' Group meeting, held September 12–13, 1995, Victoria & Albert Museum, London, www.irug.org/documents/irug2.pdf, pp. 7–20.

Lind T., Schmetzer K., Bank H. (1983) The identification of turquoise by infrared spectroscopy and X-ray powder diffraction. *Gems & Gemology*, Vol. 19, No. 3, pp. 164–168.

Miliani C., Ombelli M., Morresi A., Romani A. (2002) Spectroscopic study of acrylic resins in solid matrices. *Surface and Coatings Technology*, Vol. 151–152, pp. 276–280.

Nørbygaard T., Berg R.W. (2004) Analysis of phthalate ester content in poly (vinyl chloride) plastics by means of Fourier transform Raman spectroscopy. *Applied Spectroscopy*, Vol. 58, No. 4, pp. 410–413.

Pavese A., Prosperi L., Dapiaggi M. (2005) Use of IR-spectroscopy and diffraction to discriminate between natural, synthetic and treated turquoise, and its imitations. *Australian Gemmologist*, Vol. 22, No. 8, pp. 366–371.