DEVELOPMENTS IN GEMSTONE ANALYSIS TECHNIQUES AND INSTRUMENTATION DURING THE 2000S

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The first decade of the 2000s continued the trend of using more powerful analytical instruments to solve gem identification problems. Advances in gem treatment and synthesis technology, and the discovery of new gem sources, led to urgent needs in gem identification. These, in turn, led to the adaptation of newer scientific instruments to gemology. The past decade witnessed the widespread use of chemical microanalysis techniques such as LA-ICP-MS and LIBS, luminescence spectroscopy (particularly photoluminescence), real-time fluorescence and X-ray imaging, and portable spectrometers, as well as the introduction of nanoscale analysis. Innovations in laser mapping and computer modeling of diamond rough and faceted stone appearance changed the way gemstones are cut and the manner in which they are graded by gem laboratories.

The science of gemology has its roots in two main functions: observation and interpretation of those observations. With this approach, gemologists have developed quite effective ways of identifying gem materials, separating natural from laboratory-grown samples, and detecting various treatments. For decades, interpretation of clues seen with the refractometer, polariscope, microscope, and hand spectroscope seemed all that was necessary for the identification of most gem materials. However, the late 1970s and '80s witnessed major advances in gem synthesis methods and the application of treatments to a wider array of materials, creating a need to apply the same observational and interpretational skills to data collected with more sophisticated analytical instruments. Subsequently, infrared and UV-visible spectrometers, as well as energy-dispersive X-ray fluorescence

(EDXRF) and Raman instruments, met many of the analytical needs of gemological laboratories (Devouard and Notari, 2009; Hänni, 2009; Hainschwang, 2010). These technologies were further refined and new ones were adapted (see, e.g., figure 1) as more advances were made in gem synthesis and treatment, and as computer technology for instrument control and data collection enabled more applications.

Looking back at the two previous *G&G* retrospective technology articles (Fritsch and Rossman, 1990; Johnson, 2000), it is apparent that gemological laboratories have embraced modern analytical instruments more and more in recent years. In the gemological literature, it is common to see these instruments referred to as "advanced" or "high tech." The reality is that most of these technologies have existed for some time in research universities and other industries. In most cases, the instrumentation required modification for the nondestructive analysis of faceted gemstones. Additional challenges were involved in the collection of high-quality data from gems using these instruments. The adaptation
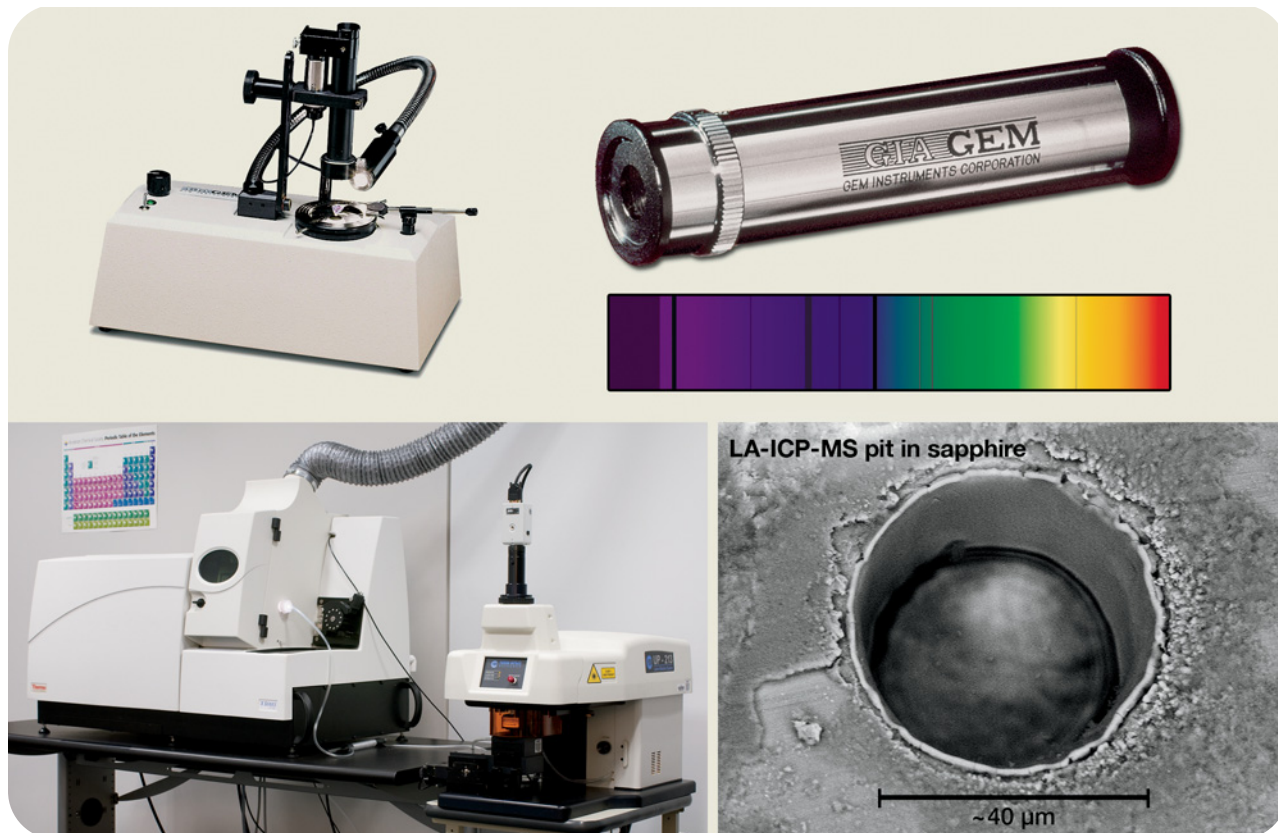
Figure 1. During the first decade of the 2000s, gemologists benefited from expanded spectroscopic capability. While they continued to use desktop and handheld spectroscopes (top) for daily identification, they also had access to information provided by high-resolution analytical instruments such as LA-ICP-MS (bottom) in the well-equipped gemological laboratory. LA-ICP-MS requires the removal of a minute amount of material for analysis, but the resulting pit is visible only with magnification (as in the SEM image seen here). Photos by Kevin Schumacher (lower left) and A. Shen (lower right).

of existing technology to gemological applications is the true innovation for gemologists.

This article surveys advances in analytical instrumentation during the first decade of the 21st century (2001–2010). The reader will see that the application of new technologies for gem analysis is an evolving process, driven by industry demands but also heavily influenced by the availability and affordability of the instrumentation.

HOW FAR WE'VE COME SINCE 2000

General Electric's introduction of HPHT treatment of diamonds at the end of the 1990s had a huge impact on the diamond industry and gemological laboratories alike. Almost overnight, we learned that colorless as well as fancy-colored diamonds could, within hours, be produced from off-color (typically brown) starting material in the same types of high-pressure, high-temperature presses used to grow synthetic diamonds (figure 2; see, e.g., Fisher and Spits,

2000; Smith et al., 2000). In many cases, there were no reliable ways for gemologists to visually distinguish these HPHT-treated diamonds from naturally colored stones (Moses et al., 1999). The effects of this treatment almost single-handedly thrust photoluminescence (PL) analysis into the gemological limelight (Chalain et al., 1999).

The early 2000s also saw huge improvements in the growth of synthetic diamonds by the chemical vapor deposition (CVD) method. Prior to this decade, the vast majority of single-crystal CVD synthetic diamonds consisted of very thin (≤1 mm) plates or coatings on seed crystals (Wang et al., 2007). By 2010, faceted colorless, brown, yellow, and pink samples up to ~1 ct were being produced by at least one U.S. company (Apollo Diamond Inc.) and were being submitted to the GIA Laboratory for grading reports. Crystals as large as 10 ct have reportedly been grown in university and research laboratories (Hemley and Yan, 2005; Wang et al., 2007, 2010). PL
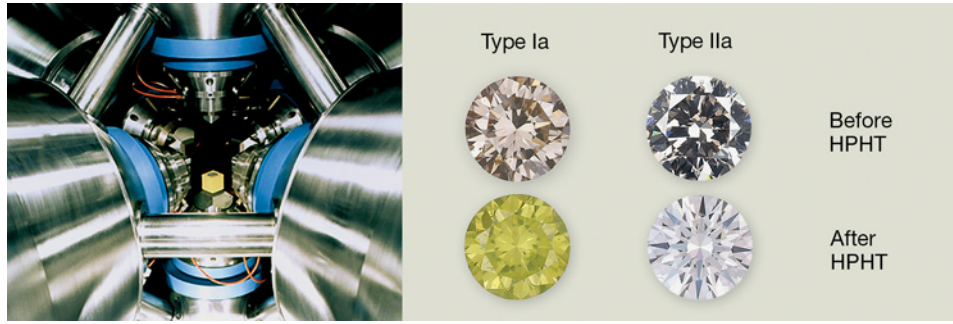
Figure 2. At the end of the 1990s, HPHT treatment of diamond using large presses (left) changed the industry forever and drove innovation in the use of analytical techniques such as photoluminescence to identify the origin of color in diamonds. Photos by Robison McMurtry.

analysis and luminescence imaging proved essential for the identification of many of these new synthetic diamonds. The DiamondView instrument, developed by De Beers in the mid-1990s (Welbourn et al., 1996), provided a practical means of imaging growth-related fluorescence patterns.

The colored stone industry was not without several critical events as well. In 2002, the undisclosed diffusion of trace amounts of beryllium into corundum nearly destabilized the sapphire trade due to the influx of large amounts of treated orange, red, and pinkish orange ("padparadscha") material (see, e.g., Emmett et al., 2003; Notari et al., 2003). Because the light element Be cannot be detected by EDXRF analysis, which was routinely used to determine chemical composition in many gemological laboratories, researchers and lab gemologists turned to laser-induced breakdown spectroscopy (LIBS) and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS).

The first decade of the 2000s also saw increased demand for country-of-origin information on lab reports for rubies, sapphires, and emeralds. Discoveries of new sources for copper-bearing tourmaline in Nigeria (2001) and Mozambique (2005) generated interest in separating these gems from those of Brazil (figure 3; see Abduriyim et al., 2006; Laurs et al., 2008). The value of trace-element analysis to country-of-origin determination further spurred the use of LA-ICP-MS in the gemological community. The demand for gem lab report services to be offered on-site at trade shows prompted the development and proliferation of portable infrared and visible-range absorption spectrometers.

This past decade also witnessed new developments in the pearl industry, including treated yellow and "chocolate" cultured pearls, the introduction of cultured conch pearls, and the proliferation of bead-less cultured pearls (Elen, 2002; Wang et al., 2006; Krzemnicki et al., 2009a; Wang et al., 2009; Karampelas et al., 2010; Krzemnicki et al., 2010).

The need to identify these products led to broader use of X-ray and luminescence imaging.

Late in the decade, a new generation of very thin colored or colorless surface coatings began to be applied to diamond, topaz, cubic zirconia, and tanzanite (e.g., Shen et al., 2007, Gabasch et al., 2008; McClure and Shen, 2008). The semiconductor industry and academic communities developed sophisti-

Figure 3. New sources of copper-bearing tourmaline were discovered in Nigeria (19.90 ct) and Mozambique (4.29 ct) in the early 2000s, driving a demand for country-of-origin certification to separate them from Brazilian Paraíba stones (2.59 ct). LA-ICP-MS analysis of trace elements in tourmaline proved to be very effective in separating these tourmalines (graph simplified from Abduriyim et al., 2006). Photos by Robert Weldon.
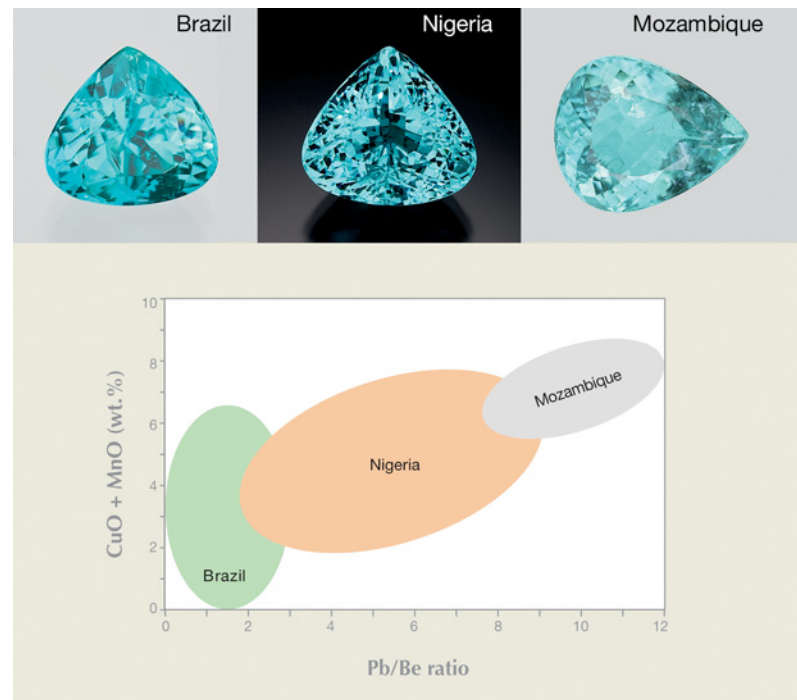
cated tools for nano-scale fabrication, coating, and analysis. This technology was then applied to a variety of gem materials as coatings and chemically modified surface layers of just a few tens of nanometers thick. While such treatments can often be identified using standard gemological observation, some are difficult for gemologists to detect.

Nano-fabrication methods to improve gemstone appearance have also been introduced recently (Gilbertson et al., 2009). In addition, the 2000s were marked by increased demand by consumers for more cut-quality information on diamond grading reports. Evaluation of cut quality became much more feasible over the last 10 years thanks to advances in gemstone facet mapping tools and automated facet and proportion measuring techniques (Moses et al., 2004).

Of course, not all the instrument technologies that were used to address gemological problems became mainstays in gem labs. Techniques such as EPR/ESR, XRD, NMR, NAA, PIXE, SEM, TEM, and others were occasionally applied for specific research needs, but due to cost, sample destruction, or limits on applications, these powerful tools have not yet seen routine use in solving gemological challenges. See the *G&G* Data Depository (gia.edu/gandg) for a list of references to studies in which these other techniques were applied to gemological problems.

CHEMICAL ANALYSIS

One of the most important advances in gemology since 2000 is the emergence of new techniques for microchemical analysis. This technology has been extensively used by the materials science and geology communities since well before 2000. Commonly the term *microchemical analysis* refers to techniques using micrometer-to-submicrometer beams of charged particles or electromagnetic radiation for localized chemical analysis, such as an electron microprobe or secondary ion mass spectrometry (SIMS). Microprobe analysis has been used in gemology for decades, while SIMS was introduced to the gem trade in the early 2000s. However, these two types of instruments have not become widely available in gemological laboratories due to their high acquisition and operating costs, and sample preparation requirements (mounting, carbon coating, etc.). The widespread use of another technique, LA-ICP-MS, greatly changed the gemological identification landscape in the first decade of the 2000s.

LA-ICP-MS. A typical quadrupole ICP-MS attached to a laser ablation unit (213 nm or 193 nm wavelength) can be acquired for a quarter the price of an electron microprobe or SIMS instrument (the latter generally costs in excess of US\$1 million). LA-ICP-MS can detect almost all chemical elements with detection limits in the range of parts per million (ppm) to even parts per billion (ppb) levels (Abduriyim and Kitawaki, 2006; Sylvestor, 2008).

An LA-ICP-MS instrument consists of three components: (1) a laser ablation unit, (2) an inductively coupled plasma torch, and (3) a mass spectrometer (figure 4). Three commonly used laser wavelengths are 266, 213, and 193 nm, the choice of which is typically determined by the primary use of the instrument. The laser physically ablates (removes) small amounts of material from a gem sample using short pulses. The typical spot size for analysis is ~40 μm in diameter (again, see figure 1), approximately half that of a human hair. The ablation depth is ~20–30 μm. The required sample amount is in the picograms (10^{-12} g) to nanograms (10^{-9} g) range, which is an extremely small amount of material

Figure 4. LA-ICP-MS consists of a laser-ablation sample introduction chamber, an inductively coupled plasma (ICP) unit, and a mass spectrometer (MS); the diagram is adapted from Masaaki (2006). Typical laser ablation spots are very small (40 μm across, see also figure 1), as seen compared to a standard laser inscription on the girdle of a sapphire (right). Photomicrograph by J. Shigley; magnified 10×.
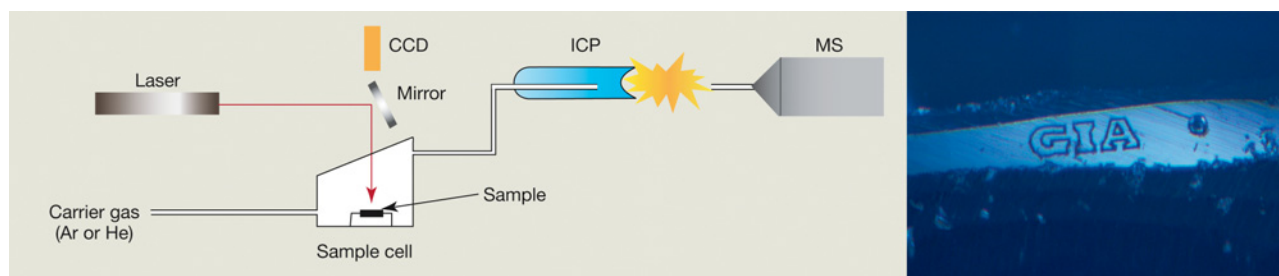
Figure 5. Beryllium-diffusion treatment of sapphire to produce padparadscha-like and other colors led to the widespread use of LA-ICP-MS in gem labs. The untreated stone is 88.11 ct and the Be-diffused sample is 2.16 ct. Photos by Kevin Schumacher (left) and Robert Weldon (center).

(i.e., <0.00000001 ct). Therefore, this method is generally considered minimally destructive.

After ablation, the vaporized material is transported by a carrier gas (usually He or Ar) to the ICP-MS where a plasma torch, typically operating at 8,000–10,000°C, ionizes the sample aerosol, causing all atomic elements present to have positive or negative charges. Once the sample is ionized, the ions are sent to the last part of the instrument, the mass analyzer (most commonly, a quadrupole mass spectrometer). The mass spectrometer separates the different ions in the plasma before they enter the detector, which measures the quantity of each ion.

One big advantage of LA-ICP-MS analysis is that it requires minimal sample preparation. In addition, it can analyze samples of almost any shape and size. Since laser pulses ablate the sample continuously, any possible surface contamination will be ablated away after a few laser pulses and does not affect the analysis. In reality, the LA-ICP-MS is analyzing a "depth profile" of a sample, beginning at the surface and extending into its interior. This feature can be advantageous for some applications, such as study of inclusions. LA-ICP-MS can be fully quantitative if a set of standards with known concentrations for the elements of interest in the same matrix is available. Also useful are some commonly available multi-element doped glass standards (see, e.g., Abduriyim and Kitawaki, 2006; Sylvestor, 2008). Without the use of such standards, the analytical results obtained by this technique must be considered semiquantitative.

As noted earlier, the introduction of LA-ICP-MS was a matter of necessity for the identification of Be-diffused sapphires (figure 5; see also Emmett et al, 2003), since traditional techniques, such as EDXRF and electron microprobe analysis, could not detect elements as light as beryllium. With its excellent detection ability (<0.2 ppm) for Be, LA-ICP-MS rapidly found its way into gemological laboratories in the 2000s.

The superior sensitivity of LA-ICP-MS to almost all elements in the periodic table has given gemologists new insights and perspectives on various gem materials. For example, data produced by this technique are now being used for country-of-origin studies on rubies, sapphires, copper-bearing (Paraíba-type) tourmalines, and emeralds (e.g., Abduriyim and Kitawaki, 2006; Abduriyim et al., 2006). In addition, many attempts were made to study trace elements in diamonds to determine their geographic origin in support of the Kimberley Process (Weiss et al., 2008; McNeill et al., 2009). However, little progress was made on this front because trace-element impurities in diamonds could not be consistently linked to geographic origin. This is probably because diamonds most often crystallize deep in the Earth's mantle. Unlike the source-specific trace elements in other gems that are often unique to particular regions (i.e., "countries") of the earth's crust, the mantle is a constantly evolving and mixing reservoir of partially molten rock beneath the crust, rendering diamond country-of-origin determination on the basis of trace elements all but impossible.

LA-ICP-MS has been used for a number of other applications, including the separation of natural and synthetic gems and the identification of pearl nuclei (e.g., Abduriyim et al., 2004; Sinclair, 2005; Wang et al., 2005; Jacob et al., 2006; Krzemnicki et al., 2007; Peucat et al., 2007; Breeding and Shen, 2010).

LIBS. This analytical method uses energy pulses from a high-energy laser to ablate small quantities of a sample. With focused laser beams, the area of abla-

tion can be just tens of micrometers wide. The ablated material is heated to such a high temperature that the atoms and ions are in an energetically excited state and emit light at characteristic wavelengths. The chemical elements present in the sample are measured by sensitive optical spectrometers positioned at the plume of ablated material.

LIBS instruments require no vacuum and typically have a microscope coupled to a video camera for precise positioning of the sample. LIBS costs less than many other instruments capable of trace-element analysis, provides rapid results, and is comparatively easy for an operator to use. Its application in gemology was motivated by the fact that LIBS is sensitive to beryllium, with detection limits of a few parts per million, so the technology was initially used to test for Be-diffused corundum (Krzemnicki et al., 2004, Abduriyim and Kitawaki, 2006). However, LIBS analyses have proved more difficult to rigorously quantify than analyses from LA-ICP-MS or SIMS, and LIBS instruments are less sensitive than the other two methods. LIBS has also been used to determine the minor and trace elements in beryl (McMillan et al., 2006a,b).

SIMS. This powerful method can analyze most elements of the periodic table with high sensitivity (parts per billion to parts per trillion). It can provide detailed compositional depth profiles near the surface of samples, even resolving chemical changes with depth at the nanometer scale, as seen in the chemical profile of a diamond surface coating shown in figure 6. While the sensitivity is excellent for most elements, the sample preparation needed is significant (see below) and the cost of analysis is high. Considerable time and effort is also necessary to produce the standards necessary for quantitative analyses. Nevertheless, SIMS is rapidly gaining importance in materials science, geoscience, and gemology (e.g., Emmett et al., 2003; Koch-Muller et al., 2006; Reiche et al., 2006; Fayek, 2009).

The analysis requires a flat surface, and the samples usually must be electrically conductive or coated with a thin layer of gold to maintain charge neutrality in the focused ion beam (typically oxygen or cesium ions). More-involved methods do exist, however, to flood nonconductive samples with electrons (negative ions) when positively charged ion beams are used. Samples are evacuated at ultra-high vacuum (10^{-10} torr) for several hours before entering the ion-beam compartment. The instrument pictured in figure 6 can accommodate samples up to 1 inch (2.5 cm) in diameter.

SIMS can measure the isotopic compositions of most elements, which opens the possibility of applying the data to country-of-origin determinations. Although seldom used in gemology today, the precise determination of isotopic ratios can be of great value in the origin determination of a wide variety of gem materials. Early studies (Giuliani et al., 2000, 2005) correlated emerald samples from a few localities with their measured oxygen isotope ratios. More recently, Giuliani et al. (2007) applied the technique to corundum, reporting that the ratio of ^{18}O to ^{16}O (expressed in units of $\delta^{18}O$) ranges between 1.3 and 15.6 parts per thousand (‰) as compared to an ocean water standard for samples of various geologic origins. For example, corundum samples from cordierite-grade metamorphic rocks had $\delta^{18}O$ of 1.7–2.9‰, whereas those from marble skarn deposits ranged from 10.7 to 15.6‰, indicating that isotopic signatures can be powerful tools for origin determination when combined with other gemological observations. It was also determined that heat treatment did not affect the oxygen isotopic values of these samples.

RAMAN AND LUMINESCENCE SPECTROSCOPY

Today, photoluminescence or UV-Vis-NIR absorption spectroscopy may be required to determine if a diamond is naturally colored or treated, and Raman spectroscopy often proves useful in colored stone identification. In most cases, a combination of spectral features and gemological properties can provide a reliable identification. In addition, the challenges presented by gem-quality CVD synthetic diamonds have made gemological laboratories more dependent on high-quality PL spectroscopy (e.g., Wang et al., 2007).

Both Raman and PL spectroscopy typically involve exciting a sample with a laser and analyzing the light given off in response. Raman scattering occurs when laser light is absorbed by the sample and, depending on the vibrational structure of the material, re-emitted (i.e., scattered) with frequencies that are shifted relative to the excitation source. Photoluminescence involves absorption of laser light, a photo-excitation process, and the dissipation of excess energy by emission of light of different wavelengths that depend on the electronic structure of defects present in the material. Most Raman spectrometers can measure photoluminescence as well as Raman scattering.

In the 2000 retrospective issue (Johnson, 2000), Raman spectroscopy and Raman libraries were dis-
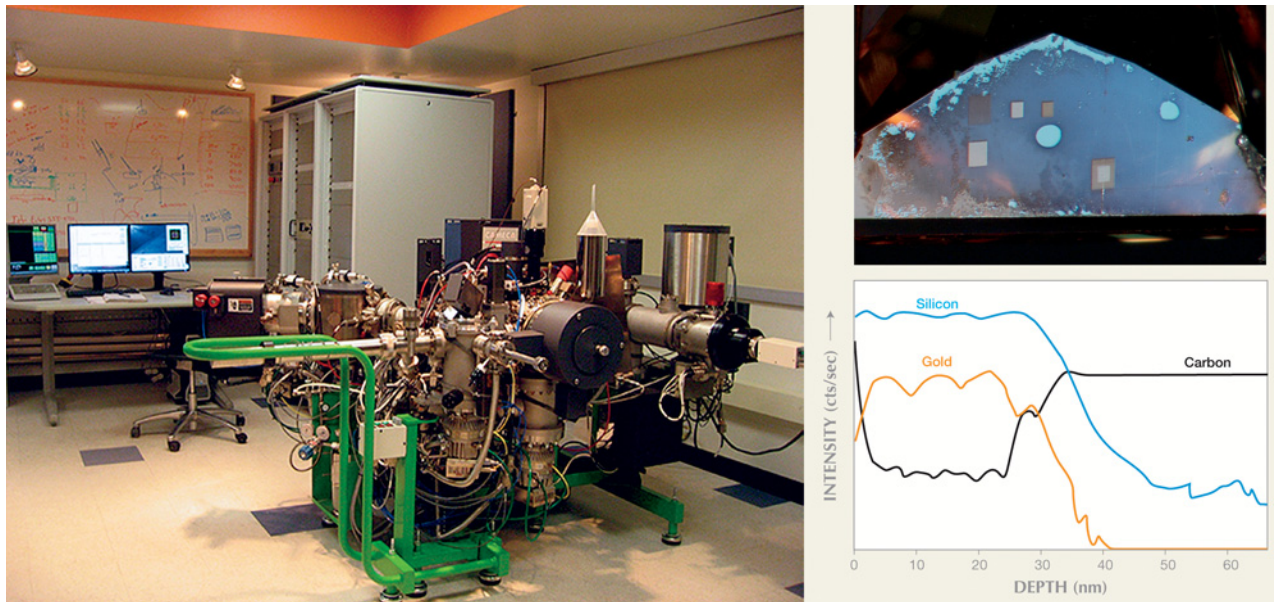
Figure 6. This Cameca IMS 7f-GEO magnetic sector SIMS instrument (left) is used at the California Institute of Technology. The ultra-high vacuum airlock through which samples are introduced is in the front left of the instrument. The mass spectrometer is to the right side, and the ion guns are at the rear-center and right side. SIMS was used to analyze the chemical composition of the coating on this facet of a pink diamond (leaving the rectangular spots on the oxidized coating seen in reflected light on the image at upper right; magnified 20×). Analysis revealed that the coating was composed primarily of Au and Si (lower right; modified from Shen et al., 2007). Photos by G. Rossman (left) and A. Shen (top right).

cussed and photoluminescence (PL) spectroscopy was mentioned briefly. At the time, the PL method did not have significant gemological applications or widespread use.

Raman. Raman spectrometers are useful for rapidly identifying gemstones, since most materials produce characteristic Raman spectra. Advances in NIR and visible lasers, charge-coupled device (CCD) detectors, and Rayleigh rejection filters have increased the detection sensitivity and decreased background fluorescence. With these advances, Raman spectra can be collected from most stones, even those with strong fluorescence reactions.

The use of Raman spectra to identify gem and other minerals requires a spectral reference library against which an unknown sample can be compared. One of the most reliable ones is the RRUFF project (Downs, 2006). See box A for a list of databases of interest to those involved with gem characterization.

Photoluminescence. Whereas Raman spectroscopy can prove that a sample is diamond, PL spectroscopy is needed to study the subtle distinctions in diamond lattice defects that are useful for distinguishing between natural, synthetic, and treated diamonds, and for determining the origin of a diamond's color. The configuration of the components within the diamond lattice—such as nitrogen, vacancies (missing carbon atoms), and out-of-position carbon—varies with a diamond's growth or temperature history. The high sensitivity of PL (typically at the parts-per-billion level) allows the detection of very subtle peaks that cannot be observed using other forms of spectroscopy (e.g., the H3 peak is rarely seen in the UV-Vis absorption spectra of colorless type IIa diamonds, but it is commonly observed in their PL spectra). Many such diamond peaks are included in Zaitsev (2003), an extensive compendium of spectral features obtained from much of the scientific diamond literature.

As an example, Fisher and Spits (along with Smith et al.) reported in 2000 on the HPHT decolorization of type IIa brown diamonds, and showed that laser-excited PL spectroscopy with the stones at liquid-nitrogen temperature (77 K) was a reliable method to identify them (see Johnson, 2000). Suddenly, PL spectroscopy was catapulted into widespread use in major gem testing laboratories, and it has since proved very helpful for detecting several types of color treatment in diamonds, including irradiation and combination treatments (e.g., Wang et al., 2005), as well as for identifying CVD synthetics (e.g., Martineau et al., 2004; Wang et al., 2007, 2010).

PL spectroscopy has also proved useful for some colored stone applications. For example, separating natural from synthetic spinel can be difficult in high-clarity gems. However, PL analysis of samples with trace or higher concentrations of chromium can easily distinguish laboratory-grown material from natural spinel (figure 7; Notari and Grobon, 2003; Shen et al., 2004; Kitawaki and Okano, 2006). Similar features provide evidence for the heat treatment of natural spinel to enhance color (Saeseaw et al., 2009). Additionally, PL analysis can be combined with Raman spectroscopy to separate natural red coral from its dyed counterpart (Smith et al., 2007).

Cathodoluminescence (CL). Cathodoluminescence is the emission of light from a material that is excited by an electron beam. The resulting luminescence can be imaged to show spatial variations in color or intensity, or it can be collected as spectra in the UV-Vis-NIR range. Depending on the type of CL instrument, the sample needs to be under vacuum (typically ~10^{-6} torr), which can significantly add to data collection time.

In many cases, photoluminescence (in the case of spectra) and the DiamondView (in the case of imaging) can provide comparable data, and these instruments are used far more frequently in gemology because the samples do not need to be under vacuum. CL has similar applications to PL since it can excite peaks that can be used to determine diamond type, examine melee (Kanda, 2006; Kanda and Watanabe, 2006), and distinguish natural from synthetic diamonds on the basis of differences in growth morphology (e.g., Shigley et al., 2004).

The major advantages of CL analysis are its ability to resolve features down to 10–20 nm and the fact it allows simultaneous collection of imaging and spectroscopic data (e.g., Yang et al., 2003). Therefore, any features observed in CL imaging may be analyzed spectroscopically.

For materials of gemological interest, CL has been used mostly on diamonds, but also on quartz (Müller et al., 2003), jade (Kane and Harlow, 2006; Ouyang et al., 2006), and sapphire (Lee et al., 2006).

Figure 7. Photoluminescence analysis of red spinel (here, 10.42 ct) can separate natural from synthetic and heat-treated samples. Spectra are offset vertically for clarity. Photo by Robert Weldon.

ADVANCES IN SPECTROMETERS AND LIGHT SOURCES

Recent developments in spectrometers and light sources have produced instruments that are highly portable and available as modular components, allowing users to customize the instrumentation to fit their needs or to reduce expenses by purchasing only the necessary equipment and spectrometer resolution. This new generation is also quite affordable, as high-quality spectra can be obtained from instruments costing as little as a few thousand dollars, depending on the application.

Spectrometers. In the last several years, the availability of spectrometers with charge-coupled device (CCD) detectors has greatly increased the speed of collecting UV-Vis-NIR absorption and fluorescence spectra (down typically from a few minutes to a few seconds), and made it possible to easily measure very short-lived phosphorescence spectra (see, e.g., Fritsch et al., 2003; Eaton-Magaña et al., 2008).

Earlier technology (such as wavelength-scanning spectrometers and spectrofluorometers) cannot record time-dependent spectra (e.g., phosphorescence), because those instruments sequentially proceed across the wavelength range by moving a prism or diffraction grating to collect spectral data. In contrast, the CCD spectrometers developed during this decade can simultaneously collect data over the entire wavelength range (although with reduced resolution for large wavelength ranges). Depending on the light source and the material being evaluated, these spectra can be collected over extremely short integration (i.e., data collection) periods.

Light Sources. In 2005, researchers studied the phosphorescence spectra of the Hope diamond (Eaton-Magana et al., 2008) using a CCD spectrometer and a broadband UV source that provided radiation in the 215–400 nm range. This broad range made it impossible at the time to distinguish the various phosphorescence reactions at short- and long-UV wavelengths unless a filter that limited the wavelength range was used. This considerably reduced the luminescence signal intensity and required a high-sensitivity, low-resolution spectrometer.

Since then, several alternative light sources have been introduced that are considerably advanced in their technology, light output, and size. UV-range LEDs have improved significantly in the last few years, and have a high energy output that enables the use of a high-resolution spectrometer and shorter integration times (figure 8). They also surpass standard gemological lamps in that they provide only a very narrow band of UV radiation. These UV sources have resulted in significant improvements in the quality of fluorescence and phosphorescence spectra.

REAL-TIME IMAGING

Imaging techniques have always been important in the analysis and identification of gems. From the face-up color to the nature of inclusions and other internal features, gems have a variety of properties that require visual representation. Thanks to advances in digital photography, the first decade of the 2000s saw the development of real-time imaging of properties such as fluorescence and X-ray transparency. Prior to this decade, these techniques were limited by long exposure requirements. Real-time imaging allows for instant visual analysis of bulk fluorescence, internal structures, and differences in luminescence between host gem and fracture-filling materials (Notari et al., 2002). Compared to conventional film-based analysis, in which only a few areas or viewing angles of a stone are typically recorded, real-time imaging allows for a more complete evaluation of the gem. In most instruments, samples can
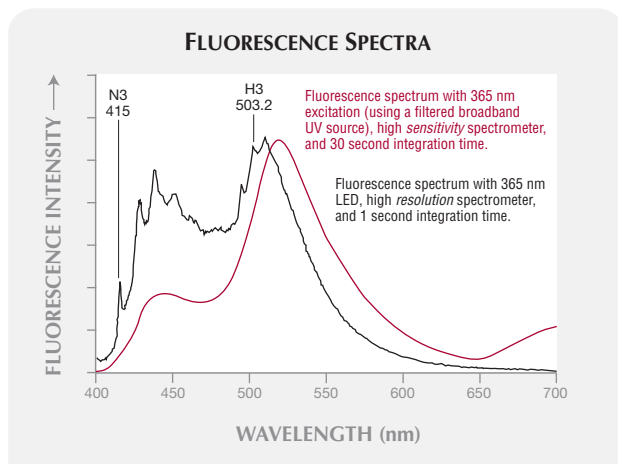
FLUORESCENCE SPECTRA

Figure 8. The fluorescence collected from analogous greenish yellow diamonds, but illuminated by different light sources, show different spectra (red spectrum, from Eaton-Magaña et al., 2007, collected June 2005; blue spectrum collected November 2009). The later-generation LED allows the use of a higher-resolution spectrometer, which reveals much finer detail, including the N3 (415 nm) and H3 (503.2 nm) zero-phonon lines and their sidebands. These narrow-band LEDs provide gemologists with a better understanding of the causes of fluorescence in gems.

be moved and rotated while images are continuously acquired and viewed. In an ever-evolving world of complex gem treatments and synthetics, subtle details seen in several orientations are often the key to identification.

DiamondView. The DTC DiamondView instrument was introduced in the 1990s for separating natural from HPHT-grown synthetic diamonds (Welbourn et al., 1996). While the instrument remains valuable for that purpose, the 2000s saw the development of several new applications. In addition to growth sectors, a number of defects can be identified that provide useful information about the thermal history of a diamond, including some indications of HPHT treatment (Breeding et al., 2006). Also, CVD

synthetic diamonds can often be identified by a characteristic pattern (figure 9).

Features seen with the DiamondView in colored stones were shown to be valuable as well. Heat treatment of ruby and sapphire can sometimes be identified from blotchy colored patterns of fluorescence, and growth lines in high-clarity flame-fusion synthetic gems can often be identified in the DiamondView because they tend to fluoresce enough to show their curved pattern even when they are not easily visible with a microscope (again, see figure 9; Breeding et al., 2006). Fracture-filling materials in many treated gems have a distinctive fluorescence when viewed with the DiamondView. For example, the type of glass filler used in ruby and sapphire can be identified from the fluorescence color: Lead-glass fillers fluoresce blue, whereas typical heating-related glass-filled fractures and cavities usually show a white fluorescence. The Diamond-View can also be used to separate oil and epoxy fillers in emeralds (Breeding et al., 2006).

X-ray Radiography and Tomography. We also saw real-time X-ray imaging applied to gem analysis during the first decade of the 2000s. X-ray techniques are particularly useful for evaluating whether pearls are natural or cultured and grown in saltwater or freshwater, by revealing details of their internal characteristics. X-radiography has long been used to reveal the growth structure and presence or absence of a bead nucleus in natural and cultured pearls. The instrumentation now allows the analyst to move the pearls and other samples laterally while viewing radiography images in real time. In addition, the X-ray detector and/or source can be moved to image different depth sections within the pearl, all while the changes are seen on a monitor (and can be captured digitally at any time). Whereas older, film-based radiography was used to collect only 1–2 image positions due to the time required to develop

Figure 9. The DTC DiamondView instrument allows for real-time imaging of fluorescence features in diamonds and other gems, such as the characteristic curved growth lines seen in CVD synthetic diamond (left) and synthetic sapphire (right). Photos by Karen Chadwick (left) and C. M. Breeding (right).
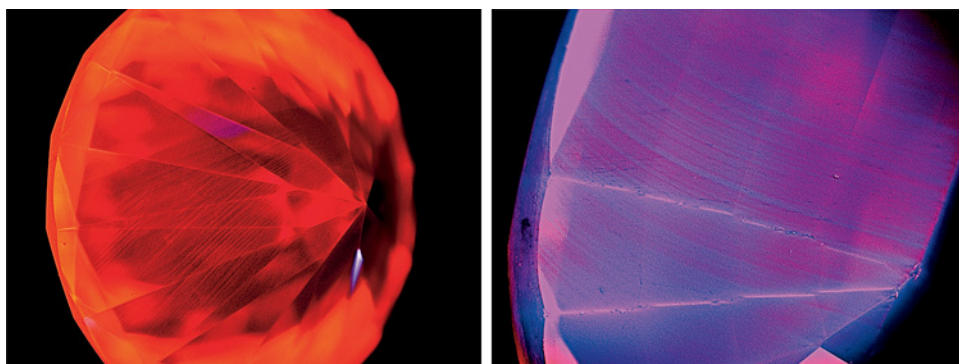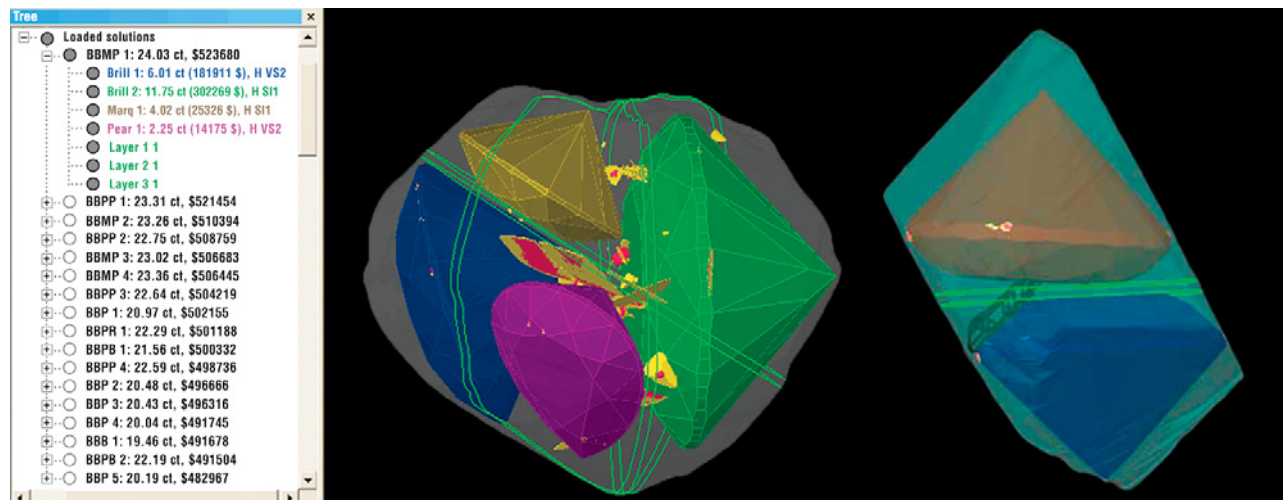
Figure 10. Software such as the Lexus M-Box has provided unprecedented opportunities for gem cutters to map their rough stones to maximize cutting efficiency. Composite image courtesy of Lexus.

the film, the newer, digital imaging systems allow for virtually unlimited images that can be adjusted as they are seen by the analyst.

Another advancement in imaging that the gemological community first used in the 2000s involves X-ray computed microtomography. This technique enables high-resolution X-ray "slices" through a rotating pearl (Krzemnicki et al., 2009a, 2010; Karampelas et al., 2010) that are then combined using specialized computer software to generate a three-dimensional (3D) representation of its internal structure. Despite long acquisition times, this type of imaging is potentially valuable for pearl identification because a single radiograph is limited by the angle at which it is collected relative to the orientation of internal features. X-ray computed microtomography overcomes that limitation by creating a full 3D rendering of the sample.

A related technique, X-ray topography, has been used to study the internal structure and growth history of diamonds (Diehl and Herres, 2004).

DIAMOND CUTTING AND EVALUATION

For centuries, it was understood that the face-up appearance of polished diamonds is related to facet arrangement and their relative angles (e.g., Moses et al., 2004). As profit margins for gem cutting have decreased, tools for planning the optimized cutting of rough diamonds have improved. Diacom, Lexus, OGI, and Sarin have introduced methods of scanning the shape and dimensions of rough diamonds, and some map inclusions as well (e.g., Sarin's new Galaxy 1000 and the Lexus M-Box; see figure 10). The Galaxy 1000 system can map inclusions in

frosted rough diamonds. Software packages help operators determine the highest value for recovery by offering various cuts and clarities, along with estimated finished carat weights. These software packages consider the grading standards of different labs, and can be adjusted to meet manufacturer-specific parameters for cutting. Various types of equipment also assist the operator in monitoring the multiple phases of the cutting process. Automatic marking, laser cutting, bruting, and polishing machines have reduced the work force needed, now that one person can monitor many machines at once.

With the advent of noncontact optical measurement tools in the 1990s, advances in computer ray-tracing, various handheld viewers, equipment to assess light performance, and computer simulations of these tools, cut grading analysis for round brilliant diamonds has gone far beyond the basic angles that were long understood by cutters. The result is the development of various cut grading systems since 2000, including:

- American Gem Society's Angular Spectrum Evaluation Tool (ASET) and cut grading system
- GIA's cut grading system
- Holloway Cut Adviser (HCA)
- HRD's cut grading system
- Imagem's VeriGem
- isee2 cut grading system
- William Bray's diamond cut scoring system

NANO-SCALE CONSIDERATIONS

For decades, gemological observations were focused on macroscopic features and microscopic details at
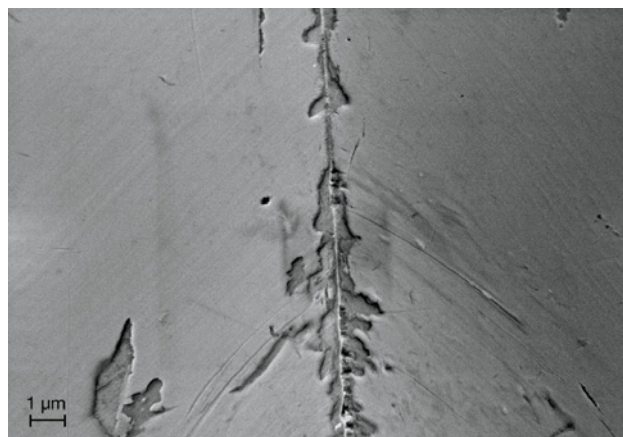
Figure 11. The early 2000s saw diamond coatings as thin as 60 nm being applied to gemstone surfaces to produce color. This SEM image shows slight wear of the coating near a facet junction on a coated pink diamond. Gemologists sometimes use this type of imaging to better understand the nature of these ultra-thin gem coatings. Micrograph by W. Wang.

the scale of millimeters or even as small as micrometers. The first decade of the 2000s, however, introduced nano-scale etching features and surface coatings to the gem industry (Rossman, 2006).

In 2009, researchers presented a method of plasma etching to create microscopic diffraction gratings on the pavilion facets of round brilliant cut diamonds (Gilbertson et al., 2009). The result was a noticeable increase in the fire seen when the diamonds were viewed face-up. The diffraction gratings were etched at the nano- to micrometer scale to separate incident white light into its spectral colors and thereby produce the new visual effect.

Also during the decade, extremely thin surface coatings were applied to a variety of gem materials (including diamond, topaz, quartz, tanzanite, and cubic zirconia) to significantly change a stone's color (figure 11) and resistance to wear. Individual coating layers, composed of elements such as Si, Ca, F, O, C, Au, Ag, Ti, Co, Fe, and Cr (Shen et al., 2007, Gabasch et al., 2008; McClure and Shen, 2008), have been measured using SIMS depth profiling analysis to be only a few tens of nanometers thick (again, see figure 6).

While most of these new nano-scale gem treatments and coatings can be detected by careful microscopic examination, some remain difficult to identify. For a better understanding of the nature of the coatings and treatments, gem laboratories have reached out to the broader research community for new techniques capable of analyzing at that scale. Many commercial companies have expressed intentions to continue refining the quality of their nanoscale treatments, so it is critical that laboratories be proactive and evaluate alternative techniques and instruments such as nanoSIMS and focused ion beam (FIB) technologies that are designed for sample preparation and analysis at the nano scale.

NanoSIMS. SIMS instruments (described above) produce an analysis spot of several tens of micrometers in diameter. In situations where smaller resolution is required, trace-element and isotopic analysis can be done on spots of a few tens of nanometers using a nanoSIMS instrument. It can analyze up to seven different masses at a time, allowing precise isotopic ratios to be determined from the same small volume. While this technology is not regularly used for gemological investigation, it has great potential for

Figure 12. Ultra-shallow diamond engravings such as GemEx's ion images (left) and the DTC Forevermark (right) were reportedly created using focused ion beams. These marks are so shallow that they require special viewers (distributed by the engravers) to be easily seen. Photo courtesy of GemEx (left) and Forevermark (right.
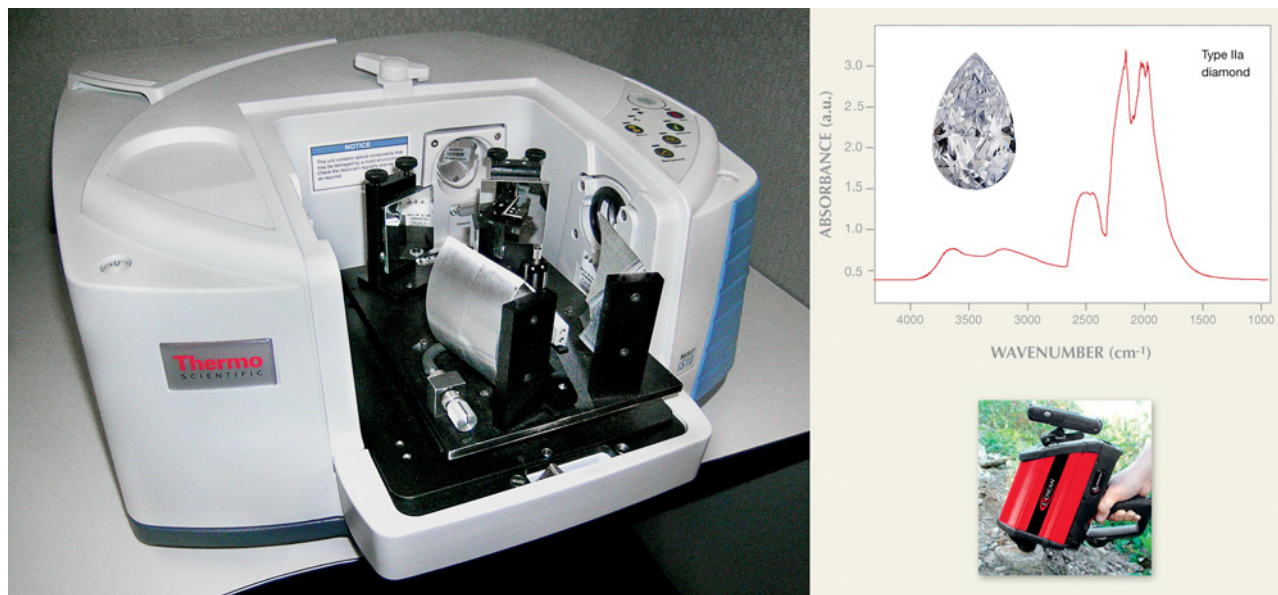
Figure 13. This Thermo iS10 FTIR (left) is one of the fast and portable desktop spectrometers often used by gemologists both in labs and at trade shows. Handheld FTIR units such as the Exoscan (lower right, designed by A2 Technologies) can be taken directly into the field to analyze gems and surrounding rocks. Both types of instruments are capable of providing valuable information about gems such as this 5.66 ct type IIa colorless diamond (upper right). Photos by C. M. Breeding (left), Robison McMurtry (upper right), and courtesy of A2 Technologies (lower right).

the identification of coatings and other nanometer-scale features of gems.

FIB. Another technology used by the semiconductor industry, FIB instruments focus a beam of ions of a chosen chemical element (usually gallium) on a target with a spot size of a few nanometers. The ion beams sputter away precise amounts of material, allowing precision milling of the target. Small, carefully controlled slices of a sample can be removed, typically for examination in a transmission electron microscope. Such slices are very useful for examining nano-scale inclusions in gems that are too small to be sampled by conventional microscopic means. The 2000s also saw the use of ion beams to create inscriptions or branding symbols on—or just under—a diamond's surface (e.g., Sheby and Cracco, 2002; figure 12).

HANDHELD AND PORTABLE SPECTROMETERS

The greater need for spectroscopic analysis in gem identification was accompanied by a desire to take the instruments "on the road." This has become particularly important for gemological labs that issue reports on-site at trade shows. In some cases, large gems or gem-encrusted artifacts at museums cannot be transported off-site for analysis, making it imperative that data be collected at the museum.

The first decade of the 2000s saw tremendous advances in the development of this portable technology. Portable (and some handheld) FTIR, UV-Vis-NIR, Raman, and EDXRF instruments all became readily available by the end of the decade. While handheld devices are not currently in widespread use in gemology, the advances in technology allow them to collect data comparable to many lab spectrometers.

Handheld FTIR instruments designed to be used in the field were equipped with diamond ATR (attenuated total reflectance) tips allowing for reflection analysis when the tip can be placed in contact with a sample. For transmission FTIR analysis, small, portable benchtop spectrometers became available. In most cases, these instruments are engineered for particular acquisition needs (i.e., the mid-infrared range) and have fixed beam splitters, higher resolution, and detectors that are electrically cooled, removing the need for a supply of liquid nitrogen for cooling (see, e.g., figure 13).

Handheld Raman instruments involved the localization of laser and optical components into a probe head that could be positioned very close to a sample, whereas tabletop Raman systems were engineered small enough to fit on a microscope (figure 14). Most handheld units have spectral resolution in the range of 7–10 cm^{-1}, which is lower than the resolutions typically used in a laboratory setting (<4 cm^{-1}), but

Figure 14. Portable desktop microRaman systems such as the Horiba XploRA (upper left) maintain most of the resolution of research-grade units, allowing for easy identification of gems such as this 2.05 ct grossular (upper right; photo by Robison McMurtry). The ability to localize Raman filters into a fiber probe (lower right; reproduced from Eckenrode et al., 2001) allows handheld units such as the FirstDefender RM (lower left; courtesy of Thermo Fisher Scientific) to be used almost anywhere.
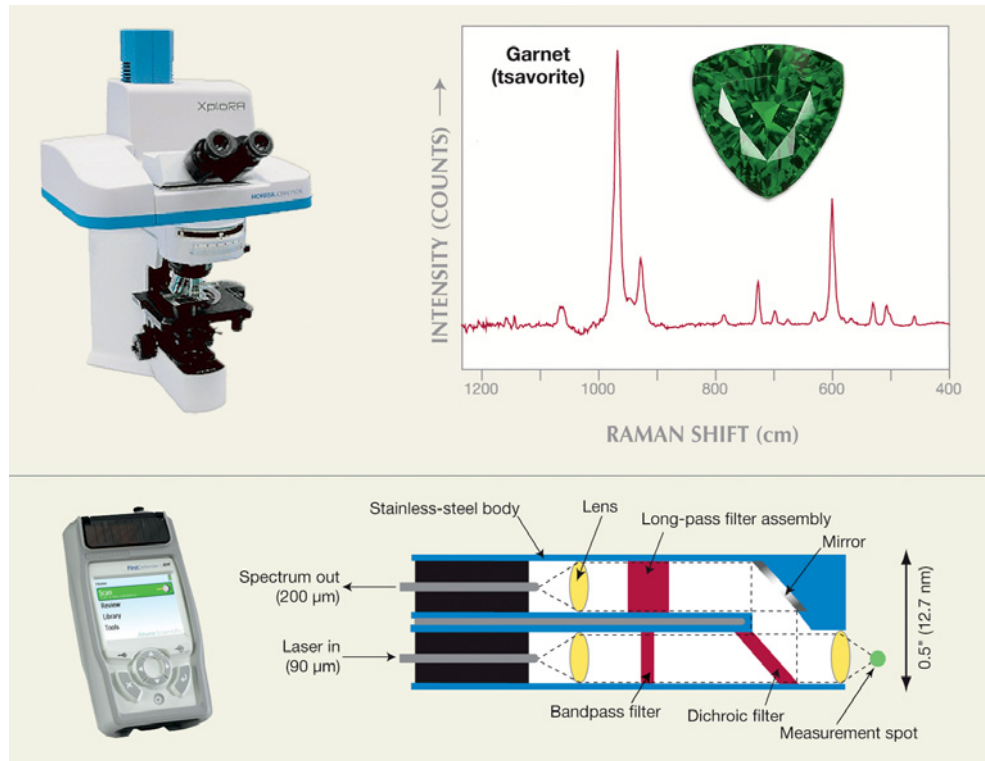
still useful for identification of materials in the field.

UV-Vis absorption spectroscopy saw the development of numerous portable units based on small, fast CCD spectrometers, which were coupled by fiber-optic cables to various light sources and fiber probes or integrating spheres to provide a relatively easy means of collecting data from gemstones (figure 15; Krzemnicki et al., 2009b). This capability is particularly important for colored stones, because the

Figure 15. Compact CCD spectrometers and light sources can be constructed into highly portable UV-Vis-NIR absorption spectroscopy units such as this one designed by SSEF (Krzemnicki et al., 2009b). Photo by M. S. Krzemnicki, © SSEF Swiss Gemmological Institute.
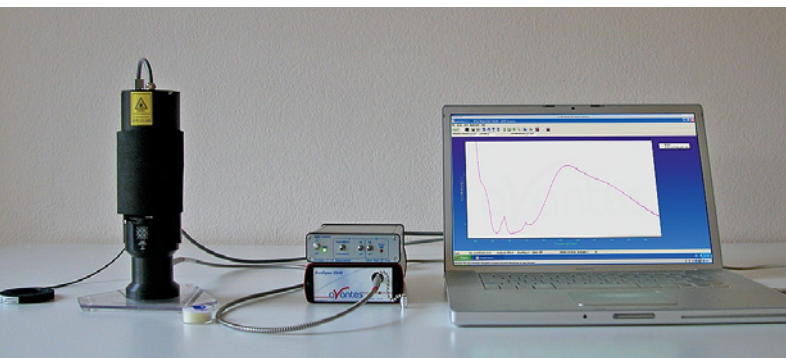
visible absorption spectrum is a direct representation of the constituents (including defects, impurities, etc.) that cause color. An additional advantage of fiber-optic cables is their use in focusing incident light directly at, and collecting transmitted light directly from, the surface of a gem. With a traditional visible-range spectrometer, a faceted gemstone scatters the transmitted light so widely in the sample compartment that only a limited percentage of it falls on the detector.

The early 2000s also saw the introduction of several handheld EDXRF analyzers (Voynick, 2010). While the elemental detection limits of these instruments are higher than their larger, laboratory counterparts, the handheld devices can be used in the field for immediate identification of the chemical composition of many gems.

While the desktop portable spectrometers generate data very similar to the data generated by their larger research-grade counterparts—which is then interpreted by a trained scientist—handheld spectrometers are typically used for field investigations and require instant data analysis and interpretation within the device itself. Thus, the quality of an analysis is often dictated by the quality of the library of reference spectra against which the data are internally compared to generate a match (particularly with Raman and FTIR spectroscopy; again, see box A). For

relevance to gemology, this means that an extensive collection of known gem materials (including rare and exotic gems, as well as synthetic and treated gem materials that are absent from most commercially available spectral libraries) must be available for analysis in order to create a comprehensive reference library. Analysis of an unknown sample in the field is of little value without such a database, so handheld instruments are often only as good as their reference libraries.

WHAT'S NEXT?

The coming decade will inevitably see improvements in the standard spectroscopic techniques (FTIR, UV-Vis-NIR, Raman) that are commonly used for gem applications (Fritsch 2006; 2007). As higher-resolution, faster, less-expensive detectors and more powerful light sources are introduced, many of these techniques will become even more important tools in everyday gem analysis. In fact, the next decade may well see small, portable spectrometers sitting alongside refractometers and microscopes on the desks of bench gemologists.

The next several years will likely include continued development and improvement of the coating techniques that were introduced in the first decade of this century. Detection of coatings on the order of a few tens of nanometers thick will require greater emphasis on surface profiling and nano-scale imaging.

A treatment that may become important in the industry is ion implantation of trace elements in gems to introduce color (e.g., Intarasiri et al., 2009). While this technique has been proved possible (e.g., figure 16), the current costs and damage to the stones have made it only a research curiosity for now. We speculate that the next decade will see refinement of this technique by treaters and the implantation of new impurities in gem surfaces. Gemological laboratories have seen very few ion-implanted samples for study, so a concerted effort is needed to characterize the results of this type of treatment before it becomes commonplace in the trade.

CONCLUSIONS

From the introduction of HPHT-treated diamonds at the end of the 1990s to the Be-diffusion of corundum in 2003 and the Cu-diffusion in feldspar over the last few years, the first decade of the 2000s was particularly challenging for the gemological community. These and other treatments, as well as advances in synthetic growth techniques (CVD, etc.), forced the development or adaptation of analytical instrumentation just to keep pace. The most significant changes came in the micro-scale chemical analysis of gems. LA-ICP-MS (and to some extent, LIBS) became mainstays in gem analysis for identifying treatments and providing reliable information about country of origin. New types of surface coatings led to the application of nano-scale analysis to gemological problems. Luminescence spectroscopy continued the breakneck pace of innovation initiated by HPHT treatment of diamonds. Raman and photoluminescence spectroscopy are now standard procedures in any gem laboratory that examines diamonds. Real-time imaging introduced a new level of viewing intricate details in pearls and fluorescence features in gems, while improvements in the portability of many instruments allowed them to be taken to museums and trade shows.

Gemology is a constantly evolving field, from the identification of treatments and synthetics to the grading of the cut quality of a faceted stone. As treatment and synthesis technology evolves to create gems or gem colors that more closely resemble their natural counterparts, the technology needed to identify them must keep pace. Gem treatment and synthesis facilities rarely provide information about their activities, so all must be inferred through careful, detailed interpretation of clues and comparison with known natu-
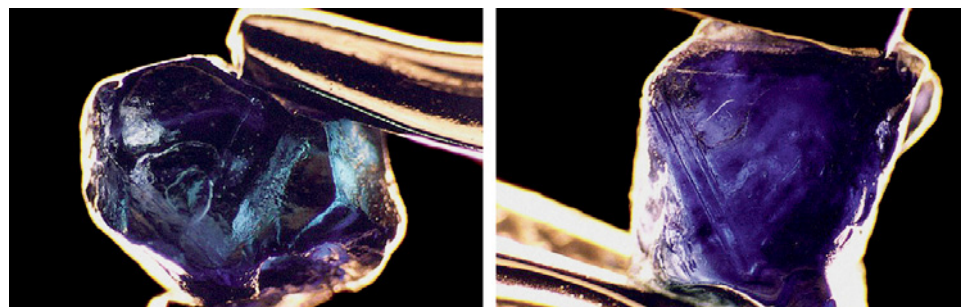
Figure 16. This sapphire from Southeast Asia is shown before (left) and after (right) treatment with ion implantation (photos from Intarasiri et al., 2009). This technique may play a role in color treatment in the coming decade.

ral, synthetic, and treated samples. In addition, most natural gems show tremendous variability, often rendering large spreads in analytical results and some uncertainty in interpretation. Nevertheless, the global gemological community has long managed to meet these challenges through a continued commitment to research. This commitment is the driving force behind the significant advances in the application of new technology to gem identification witnessed during the first decade of the 2000s.

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Key to abbreviations: *Gems & Gemology = G&G*; *Revue de Gemmologie a.f.g. = Rev. de Gem.*

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