FLUORESCENCE SPECTRA OF COLORED DIAMONDS USING A RAPID, MOBILE SPECTROMETER

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Numerous natural-color colored diamonds from the Aurora Butterfly of Peace and other collections were studied using a new type of fluorescence spectrometer that has many advantages for gemological research, including high portability, low cost, and rapid collection times. For comparison, 10 irradiated diamonds were also studied. With only two exceptions, the natural-color diamonds could be separated into three categories—based on the peak wavelength and shape of the fluorescence spectra—that *generally* corresponded to their bodycolors: (1) ~450 and ~490 nm, recorded mainly for pink, yellow, and fancy white diamonds; (2) ~525 nm, mainly for green-yellow or yellow-green and brown diamonds; and (3) ~550 nm, mainly for orange, gray-green (including chameleon), and type Ia blue-gray or gray-blue diamonds. A spectrum that is anomalous for the diamond's bodycolor may indicate that it has been treated, and in some cases, fluorescence spectroscopy can help determine diamond type.

Prior fluorescence studies performed at GIA found that about 35% of near-colorless gem diamonds fluoresce to long-wave UV radiation, with 97% of those diamonds showing blue fluorescence (Moses et al., 1997). However, colored diamonds more commonly show fluorescence, and in a wider variety of colors (e.g., figure 1). Given the methodology with which fluorescence is typically observed, it is sometimes difficult to determine the underlying mechanism of this behavior and, specifically, the influence of the natural, synthetic, or treated nature of the diamond on its fluorescence.

Becquerel (1868) and Dyer and Matthews (1958) were among the first scientists to study the fluorescence properties of diamonds. Dyer and Matthews studied the luminescence of the 415.5 and 504.0 nm systems (now identified as the N3 and H3 defects; see, e.g., Collins, 1982a) and found that these features were related to blue and green fluorescence, respectively. A review by Fritsch and Waychunas (1994) detailed the observed fluorescence and phosphorescence of diamonds according to their bodycolor.

While a large number of peaks and defect centers have been chronicled in natural diamonds using UV-Vis absorption, cathodoluminescence, and photoluminescence spectroscopy (see, e.g., Zaitsev, 2001), spectral data for fluorescence and phosphorescence are limited in the gemological literature, since luminescence is typically described by visual observations (again, see Fritsch and Waychunas, 1994). However, visual assessment of fluorescence and phosphorescence tells only part of the story. The color discerned by the unaided eye may represent a combination of two or more wavelength regions. For example, Anderson (1960) asserted that although most fluorescing diamonds appear to luminesce blue, a yellow or green component may be present but masked by the stronger blue emission. He used color filters and a spectroscope to try to identify some of the relevant

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GEMS & GEMOLOGY, Vol. 43, No. 4, pp. 332–351.

Figure 1. The colored diamonds in the Aurora Butterfly of Peace were assembled over a 12-year period by Alan Bronstein and Harry Rodman of Aurora Gems Inc., New York (these photos date from 2005). The 240 stones (0.09–2.11 ct; total weight of 166.94 carats) show nearly the full spectrum of color and cut styles available in natural colored diamonds. The collection is shown here in standard daylight-equivalent illumination (left) and long-wave UV radiation (right). Photos by Robert Weldon.

peaks. Also, a spectral peak may exhibit a long tail that will cause the observed color to differ from that of other diamonds in which fluorescence is constrained to a narrower wavelength range.

The gem collection at the Smithsonian Institution's National Museum of Natural History provided an opportunity to study the fluorescence and phosphorescence characteristics of a wide variety of colored diamonds. The materials came from the permanent collection, including the DeYoung Red and the DeYoung Pink, along with a temporary exhibit of the Aurora Butterfly collection (Solotaroff, 2003; "Rodman, Bronstein…," 2005; Eaton-Magaña, 2006a; again, see figure 1), which is a suite of 240 colored diamonds that had been loaned to the museum by Alan Bronstein and Harry Rodman of Aurora Gems. Additionally, we examined some natural and treated diamonds from GIA collections. The luminescence properties of 67 natural-color blue diamonds, including the Hope Diamond and the Blue Heart, are discussed in separate publications (Eaton-Magaña et al., 2006b, 2008).

The present study also provided an opportunity to test a new-generation charge-coupled device (CCD) spectrometer for the routine measurement of fluorescence and phosphorescence spectra of gem diamonds. This spectrometer is highly mobile (it is about the size of a deck of playing cards), extremely durable, easy to set up in minutes, permissive of rapid data collection, and relatively inexpensive (see box A for more information).

MATERIALS AND METHODS

Samples. This article provides fluorescence results for 72 colored diamonds: 62 natural, untreated (as indicated on their gem laboratory reports) and 10 irradiated (table 1). Nine of the natural-color and one of the treated samples were rough; all of the others were faceted. Most of the diamonds (48) were selected from the Aurora Butterfly collection, and the remainder came from GIA collections (22) and the National Gem Collection (2). We selected the samples according to the rarity of their bodycolor (e.g., purple and red) or the presence of visual fluorescence across the range of bodycolors. Therefore, this is not a random sampling of colored diamonds, and general statistics of fluorescing vs. nonfluorescing diamonds should not be inferred from these data. Our intent was to detect trends that might be useful for colored

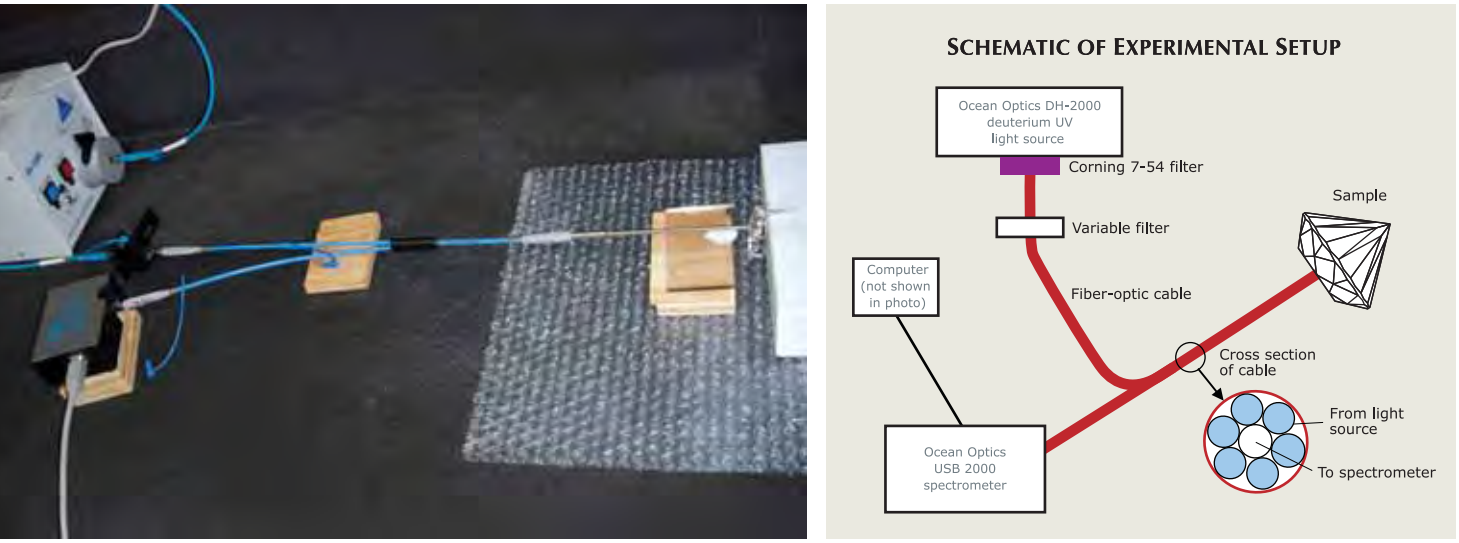


Figure 2. This photo and diagram illustrate the components of the mobile instrument (composed principally of Ocean Optics equipment) used for fluorescence and phosphorescence spectroscopy. When phosphorescence spectra were recorded, the Corning 7-54 filter and the variable filter were removed. Photo by S. Eaton-Magaña.

diamond characterization and, ultimately, identification. The very slightly yellow (G-to-I grade; Fryer and Koivula, 1986) 127 ct Portuguese Diamond was also examined to provide an example of how fluorescence intensity is related to the size of a diamond.

At GIA and the Smithsonian, all samples were tested for visible fluorescence and phosphorescence using standard 4-watt long- and short-wave UV lamps. The color descriptions in table 1 were taken from grading reports issued by gemological laboratories. For the purposes of this article, the diamonds are assigned a "key bodycolor" (see table 1) according to their dominant bodycolor, although each group may include various modifying hues. For example, within the pink color group, most were graded solely as pink, and a few were purplish pink or reddish purplish pink. Due to the variety of fluorescence results, diamonds with a green component are sorted according to their specific (dominant plus modifying hue) color description. Several diamonds graded as green-yellow to yellow-green are grouped together (key bodycolor given as yellow-green). Similarly, three diamonds graded as blue-gray or gray-blue are grouped together (key bodycolor given as blue-gray).

Fluorescence and Phosphorescence Spectroscopy. The instrumentation used to measure fluorescence and phosphorescence spectra consisted of a deuterium lamp UV source (215–400 nm), filters to control the wavelengths of incident light, a sample holder, a fiber-optic bundle to deliver incident light and collect the emitted signal, an Ocean Optics USB 2000 CCD spectrometer, and a computer (see figure 2). The UV source used for most of the fluorescence and phosphorescence spectroscopic measurements was an Ocean Optics DH-2000. The UV radiation was filtered to ~250–400 nm, and was transferred through a bundle of six optical fibers (600 µm diameter each). A seventh fiber in the core of the bundle channeled the emitted light from the diamond to the spectrometer (figure 2, right). The tip of the fiber-optic bundle was placed directly in contact with the table of each sample, which enabled us to illuminate and measure approximately equivalent volumes of each sample. Thus, we were able to compare relative intensities of signals from a wide range of sample sizes. The CCD spectrometer used in these experiments is described further in box A.

For the fluorescence measurements (again, see figure 2, right), we used a Corning 7-54 filter to block visible light (~400–650 nm) from the deuterium UV source and a variable filter (Ocean Optics LVF-HL) to deliver only a narrow band (full width at half maximum [FWHM] = 22 nm) of UV radiation to the sample. This narrow band was varied between 250 and 400 nm (e.g., figure 3). The fluorescence recorded by the spectrometer at each excitation wavelength was collected for 30 seconds. Since excitation intensity varied with wavelength (again, see figure 3), the measured fluorescence spectra were scaled uniformly over the wavelength range. Except for one sample to monitor the change, no radiometric (i.e., wavelength-dependent) calibration

BOX A: THE MOBILE CCD SPECTROMETER

The Ocean Optics USB 2000 CCD spectrometer measures wavelengths from 340 to 1020 nm and has a 200 µm slit width that provides a 10-nm FWHM resolution. This small mobile spectrometer was configured for exceptional sensitivity of broad spectral structures so that phosphorescence decay could be measured. The accuracy of the spectrometer's wavelength position was confirmed using the 435.8 and 546.1 nm lines from a mercury lamp. However, for the majority of the data, the spectrometer was not radiometrically calibrated, which would adjust the relative intensities obtained across the wavelength range. We have elected to provide the uncorrected data (i.e., the direct output from the spectrometer), as these are the spectra most likely to be produced by others using this type of instrumentation.

The CCD spectrometer was initially selected for the blue diamond study reported in Eaton-Magaña et al. (2006b, 2008), because its ability to resolve low-intensity luminescence allowed the collection of time-resolved phosphorescence spectra. In addition, the portability and ease of use enabled us to take the instrument to the gems, providing access to many more stones than would otherwise have been possible. The experimental apparatus shown in figure 2 was easily transported to and quite effectively used in the vaults of the Smithsonian Institution and in the business office of a diamantaire. When fitted with appropriate filters, the spectrometer proved effective for rapidly recording fluorescence spectra, permitting the study of a large number of colored diamonds within the limited time constraints of their availability. Nevertheless, it should be noted that this CCD spectrometer might be inappropriate for investigations that require the higher resolution of traditional research spectrofluorometers.

An important strength of the Ocean Optics spectrometer is that the fiber tip, when placed on the table of the stone, illuminates approximately similar volumes for each stone. Therefore, comparison of relative intensities is a reasonable possibility and likely more so than when luminescence is measured through a stone or from multiple facets of a stone as occurs in traditional measurements. We were able to compare the measured fluorescence intensities of the diamonds tested with this equipment since we used a consistent configuration and testing method; however, we do not feel that the *absolute* intensities we obtained could be reliably compared to data collected using similar experimental setups.

Comparison of the mobile CCD spectrometer with a standard spectrofluorometer revealed some distinct advantages and disadvantages. Speed is one advantage of the CCD instrument: The spectrofluorometer took four hours to collect the series of spectra for each sample shown in figures 7 and 11, whereas the CCD spectrometer generated its spectra in mere seconds. Additionally, a spectrofluorometer cannot record time-dependent spectra, such as phosphorescence spectra, because the instrument slowly scans across the wavelength range. The CCD spectrometer is ideal for collecting such spectra, as data for the entire wavelength range may be collected simultaneously over integration periods as short as 0.5 second.

Figure A-1. The latest CCD spectrometer from Ocean Optics, the USB 4000, is an updated version of the model used for this study. Courtesy of Ocean Optics, Inc.

The spectral resolution of the CCD spectrometer is lower than that of the spectrofluorometer and most other standard spectroscopy equipment available in a gemological laboratory, as smaller peaks typically are obscured by dominant bands, and in most cases only the general shape of the band is provided. Consequently, spectra obtained using the Ocean Optics system may need to be cross-referenced initially with other spectroscopic methods to fully analyze the defects causing the observed fluorescence.

Last, but of singular importance for small labs especially, the CCD spectrometer is quite economical. The latest model (figure A-1) currently sells for about $2,300.

TABLE 1. Summary of fluorescence results for 62 natural-color and 10 treated-color diamonds examined for this study, organized by fluorescence category.

Sample	Color	Weight (ct)	Shape	Other spectroscopy[a]	Observed long-wave UV fluorescence[b]	Key bodycolor group	Fluorescence spectra peak category	Peaks (nm) observed with 350 nm excitation (dominant peak in bold type)
Natural-Color Diamonds: Category 1								
B55[c,d]	Pink	0.48	Pear	nt	Strong blue	Pink	1	**450**, 490
B58	Pink	0.44	Pear	nt	Strong blue	Pink	1	**450**, 486
B59[d]	Purplish pink	0.36	Pear	nt	Strong blue	Pink	1	**451**, 488
B121	Deep pink	0.53	Marquise	nt	Weak blue	Pink	1	**451**, 491
B224	Reddish purplish pink	0.67	Marquise	nt	Very weak blue	Pink	1	**460**, 500
B226	Pink	0.42	Pear	nt	Moderate blue	Pink	1	**450**, 490
DeYoung Pink[d]	Fancy Light purplish pink	2.09	Pear	nt	Very strong blue	Pink	1	**460**, 485
GIA 12172-9	Faint pink	0.16	Rough	UV-Vis-NIR, FTIR	Moderate chalky blue	Pink	1	**450**, 490
GIA 21194	Pink	0.42	Rough	UV-Vis-NIR, FTIR	Moderate blue	Pink	1	**450**, 484
GIA 21232	Deep pink	0.61	Rough	UV-Vis-NIR, FTIR	Moderate greenish blue	Pink	1	**450**, 485
B1	Intense yellow	1.47	Trillion	nt	Weak blue	Yellow	1	**450**, 490
B157	Yellow	1.04	Oval	nt	Moderate blue	Yellow	1	**453**, 495
B173[d]	Yellow	1.06	Half-moon	nt	Weak blue	Yellow	1	**453**, 495
B43[d]	Fancy white	1.93	Pear	FTIR	Moderate blue	Fancy white	1	**450**, 497
B146	Fancy white	2.11	Pear	FTIR	Moderate blue	Fancy white	1	**450**, 485
B223[d]	Fancy white	1.92	Marquise	FTIR	Weak blue	Fancy white	1	**450**, 500
B190	Gray green (chameleon)	0.88	Marquise	FTIR	Moderate white	Gray-green (incl. chameleon)	1	**450**, 490
B11	Green	1.15	Cushion	nt	Moderate blue	Green	1	**450**, 490
Natural-Color Diamonds: Category 2								
B17	Yellow-green	0.55	Radiant	nt	Strong yellowish green	Yellow-green	2	441, **526**
B96[e]	Green-yellow	0.97	Oval	nt	Strong green-blue	Yellow-green	2	449, **518**
B137	Yellow-green	1.20	Pear	nt	Very strong green	Yellow-green	2	525
B194	Green-yellow	0.51	Oval	nt	Very strong green	Yellow-green	2	445, **527**
B213	Yellow-green	0.46	Marquise	nt	Strong green	Yellow-green	2	447, **523**
B236[f]	Intense green-yellow	0.91	Radiant	nt	Very strong greenish blue	Yellow-green	2	445, **523**
B239[f]	Intense green-yellow	1.03	Radiant	nt	Very strong green	Yellow-green	2	446, **524**
B98	Brown	0.54	Round	nt	Moderate red	Brown	2	510
B100	Greenish orangy brown	1.40	Pear	nt	Weak yellowish green	Brown	2	520
B167	Yellowish brown	0.76	Marquise	nt	Weak yellowish green	Brown	2	450, **520**
GIA 12172-1	Yellowish brown	0.66	Rough	UV-Vis-NIR, FTIR	Very strong orange	Brown	2	532
GIA 12172-5a	Pinkish orangy brown	0.40	Rough	UV-Vis-NIR, FTIR	Moderate orangy yellow	Brown	2	520
GIA 12172-5b	Orangy brown	0.26	Rough	UV-Vis-NIR, FTIR	Very strong yellow	Brown	2	525
B16[d]	Violet	0.31	Shield		Inert	Violet	2	445, **524**
GIA 12172-2	Faint yellow	0.58	Rough	UV-Vis-NIR, FTIR	Moderate chalky blue	Yellow	2	450, **520**
Natural-Color Diamonds: Category 3								
B13	Gray-blue	0.31	Heart	FTIR	Strong green	Blue-gray	3	530
B31	Gray-blue	0.58	Round	FTIR	Moderate blue	Blue-gray	3	450, **530**
B187[d]	Blue-gray	0.62	Marquise	FTIR	Weak blue	Blue-gray	3	532
B163	Violet	0.36	Pear		Weak green	Violet	3	535
B24[d]	Gray-green	0.34	Round	FTIR	Strong yellowish white	Gray-green (incl. chameleon)	3	450, **547**
B32	Gray-green (chameleon)	1.74	Round	FTIR	Moderate chalky yellow	Gray-green (incl. chameleon)	3	450, **545**
B70	Gray-green (chameleon)	1.01	Half-moon	FTIR	Strong orangy yellow	Gray-green (incl. chameleon)	3	555
B87	Gray-green (chameleon)	1.00	Marquise	FTIR	Strong yellowish white	Gray-green (incl. chameleon)	3	450, **542**
B127	Gray-green (chameleon)	0.31	Round	FTIR	Moderate orangy yellow	Gray-green (incl. chameleon)	3	553

Sample	Color	Weight (ct)	Shape	Other spectroscopy[a]	Observed long-wave UV fluorescence[b]	Key bodycolor group	Fluorescence spectra peak category	Peaks (nm) observed with 350 nm excitation (dominant peak in bold type)
Natural-Color Diamonds: Category 3 (cont.)								
B184	Gray-green (chameleon)	0.95	Pear	FTIR	Moderate yellow	Gray-green (incl. chameleon)	3	555
B231[e]	Chameleon	0.79	Kite	FTIR	Strong yellow	Gray-green (incl. chameleon)	3	449, **548**
B234	Chameleon	1.37	Oval	FTIR	Strong yellow	Gray-green (incl. chameleon)	3	450, **555**
GIA 12172-8b	Gray-green	0.52	Rough	UV-Vis-NIR, FTIR	Moderate orange-yellow	Gray-green (incl. chameleon)	3	540
GIA 487947202	Fancy Dark grayish yellowish green (chameleon)	0.70	Pear	UV-Vis-NIR, FTIR	Moderate yellow	Gray-green (incl. chameleon)	3	450, **548**
GIA 487988302	Fancy brownish greenish yellow (chameleon)	2.11	Heart	UV-Vis-NIR, FTIR	Very strong orangy yellow	Gray-green (incl. chameleon)	3	558
GIA 488015402	Fancy Deep brownish greenish yellow (chameleon)	0.65	Rectangle	UV-Vis-NIR, FTIR	Very strong orangy yellow	Gray-green (incl. chameleon)	3	554
B2	Brownish yellow-orange	1.02	Emerald	nt	Moderate yellowish orange	Orange	3	540
B33	Vivid yellow-orange	1.17	Pear	nt	Strong yellow-orange	Orange	3	555
B56	Vivid yellowish orange	1.67	Oval	nt	Moderate yellow-orange	Orange	3	552
B72	Yellowish orange	0.77	Round	nt	Moderate yellow	Orange	3	450, **546**
B78	Brownish yellow-orange	0.63	Round	nt	Weak orange	Orange	3	560
B166	Yellow-orange	0.81	Oval	nt	Moderate orange	Orange	3	545
B218	Orange	0.45	Pear	nt	Very strong orange	Orange	3	450, **548**
GIA 12172-8a	Yellowish orange	0.19	Rough	UV-Vis-NIR, FTIR	Moderate whitish orange	Orange	3	535
Other Natural-Color Diamonds								
B172	Yellow-orange	0.52	Round	nt	Weak brownish orange	Orange	Other	610
B181	Yellow-orange	0.58	Round	nt	Very weak brownish orange	Orange	Other	608
B39	Purple	1.60	Oval	nt	Inert	Purple	Inert	None
B232	Purple	0.17	Oval	nt	Inert	Purple	Inert	None
DeYoung Red[e]	Brownish red	5.03	Round	nt	Very weak yellow	Red	Inert	None
Treated-Color Diamonds								
GIA 21503	Green	0.31	Round	FTIR	Inert	Green	1	**450**, 490
GIA 21506	Bluish green	0.20	Round	UV-Vis-NIR, FTIR	Inert	Green	2	460, **520**
GIA 21509	Bluish green	0.42	Round	UV-Vis-NIR, FTIR	Strong blue	Green	1	**450**, 490
GIA 21510	Green	2.05	Round	FTIR	Inert	Green	1	**450**, 495
GIA 21512	Green	0.32	Round	UV-Vis-NIR, FTIR	Strong blue	Green	1	**450**, 490
GIA 21513	Greenish blue	0.26	Round	UV-Vis-NIR, FTIR	Weak bluish green	Blue	1	**450**, 487
GIA 21518	Green	0.26	Rough	FTIR	Inert		1	**450**, 490
GIA 21542	Greenish yellow	0.39	Marquise	UV-Vis-NIR, FTIR	Moderate greenish blue	Yellow-green	2	450, **525**
GIA 22020	Greenish yellow	0.44	Round	UV-Vis-NIR, FTIR	Strong greenish yellow	Yellow-green	2	444, **525**
GIA 22700	Brownish orangy yellow	0.90	Round	FTIR	Inert	Yellow	2	523

[a] For all samples tested by FTIR, the diamonds were classified as type Ia. Abbreviation: nt = not tested.

[b] Observed using standard long-wave UV lamps.

[c] A map showing the location of the diamonds in the Aurora Butterfly collection as they correspond to figure 1 is provided in the G&G Data Depository.

[d] This diamond showed blue fluorescence when examined with the DiamondView instrument.

[e] This diamond showed blue fluorescence, accompanied by areas of green, when examined with the DiamondView instrument.

[f] This diamond showed green fluorescence when examined with the DiamondView instrument.

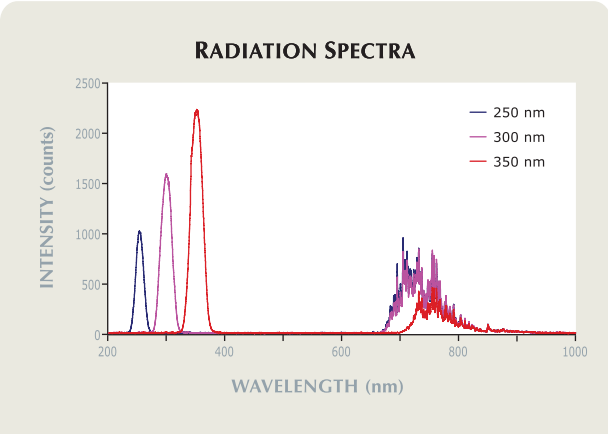


Figure 3. This plot shows the spectra of radiation used to excite the diamonds for the fluorescence spectroscopy measurements. A Corning 7-54 filter removes the light in most of the visible region of the spectrum (~400–650 nm). A variable filter further reduces the light to a narrow band in the UV region. The position of the variable filter determines the wavelength of maximum intensity of the UV radiation. Shown here are three experiments using an empty sample chamber with the variable filter positioned to give 250, 300, and 350 nm as the peak intensity. Unfiltered light is present at wavelengths higher than 650 nm.

was performed. Despite the filters, in some cases the spectra contained second-order artifacts (i.e., at twice the excitation wavelength) that were caused by the spectrometer grating.

The filters were removed for the phosphorescence measurements, because the filtered incident UV radiation necessary to perform the fluorescence measurements was insufficient to excite measurable phosphorescence in many of the diamonds. (Similarly, some samples might have exhibited fluorescence that was too weak for this system to detect.) The phosphorescence spectra were collected after an exposure period of 20 seconds; our initial testing indicated that longer exposure times did not yield significantly better results. During decay, the spectra were collected over integration times of 0.5, 1, and 2 seconds.

For the purpose of describing the fluorescence, we assigned intensity designations relative to the entire dataset. The empirical boundaries we used to describe fluorescence strength were based on the peak intensity over the 30-second collection period: *very weak* (<20 counts), *weak* (20–100 counts), *moderate* (100–600 counts), *strong* (600–1000 counts), and *very strong* (>1000 counts). These descriptors generally correspond to visual perceptions of fluorescence intensity.

At GIA in Carlsbad, we used a Thermo Aminco Bowman II Luminescence spectrofluorometer to investigate the fluorescence spectra of four diamonds (GIA nos. 12172-5b, 12172-8b, 21194, and 21542) to provide a comparison with the measurements made using the Ocean Optics equipment. Fluorescence was excited at wavelengths ranging from 220 to 400 nm (5 nm intervals), and the fluorescence spectra were recorded in the 370–750 nm range (1 nm resolution).

DiamondView Imaging. Fourteen samples were examined with the DiamondView instrument, which uses ultra-short-wave UV radiation at <230 nm, and the resulting fluorescence and phosphorescence were imaged using a CCD camera. We wished to compare the results obtained with ultra-short-wave UV to those from conventional UV lamps. Additionally, the DiamondView should illustrate any spatial differences in the observed fluorescence spectrum. The samples imaged by DiamondView were randomly selected from the Aurora Butterfly collection.

Absorption Spectroscopy. To assess the identity of the fluorescence bands, we measured ultraviolet–visible–near infrared (UV-Vis-NIR) and Fourier-transform infrared (FTIR) spectra that would better show the defects present in the diamonds.

We obtained UV-Vis-NIR spectra on most of the 22 samples from the GIA collections (see table 1) at the GIA Laboratory in Carlsbad using a Thermo-Spectronic Unicam UV500 spectrophotometer over the range of 250–850 nm with a sampling interval of 0.1 nm. The faceted samples were cooled in a cryogenic cell using liquid nitrogen and oriented with the beam passing through the girdle plane.

We recorded FTIR spectra on all 22 diamonds from the GIA collections at GIA Carlsbad and on 15 diamonds from the Aurora Butterfly collection at GIA New York (see table 1). Spectra were collected in the mid-infrared range (6000–400 cm^{-1}, at 1 cm^{-1} resolution) at room temperature with a Thermo-Nicolet Magna IR 760 FTIR spectrometer at GIA in Carlsbad and a Thermo-Nicolet Nexus 670 FTIR spectrometer at GIA in New York. We ran a total of 1,024 scans per sample to improve signal-to-noise ratios. The concentrations of A and B aggregates were calculated from these spectra using an algorithm derived from Kiflawi et al. (1994) and Boyd et al. (1995). The FTIR spectra were baseline corrected and normalized using the two-phonon region of a type IIa diamond.

RESULTS

The results of the spectroscopic measurements are described below according to three main categories of diamonds that exhibit similar fluorescence spectra at long wavelengths. In most cases, these categories corresponded well to the diamonds' bodycolors, which are discussed within each grouping. FTIR and UV-Vis-NIR spectroscopic data are also described below. Phosphorescence spectra for these samples, and for an additional 32 natural-color diamonds from the Aurora Heart and Aurora Butterfly collections, can be found in the *G&G* Data Depository at www.gia.edu/gemsandgemology. A summary of the phosphorescence results for the natural-color diamonds is reported in box B.

Category 1: Fluorescence Spectra with Dominant Peaks at ~450 and ~490 nm. All diamonds described in this section showed similar fluorescence spectra (see, e.g., figure 4). Most of the natural-color diamonds had yellow, fancy white, and pink bodycolors, but one green and one gray-green natural-color diamond also followed this fluorescence pattern. Six irradiated diamonds also showed this fluorescence pattern with weak-to-moderate intensity; they had green to greenish blue bodycolors.

All 10 pink diamonds, including the DeYoung Pink, showed moderate fluorescence with peak intensity at ~450 and ~490 nm. One pink diamond examined with the high-resolution spectrofluorometer (GIA 21194) showed the zero-phonon line (ZPL) at 415 nm related to the N3 defect and its lower-energy (higher-wavelength) sideband.

In general, most yellow diamonds show weak or no fluorescence; of those that do fluoresce, blue has been reported as the dominant color (King et al., 2005). Here, three of the four natural-color yellow diamonds without a greenish component exhibited moderate-to-strong fluorescence with peaks at ~450 and ~490 nm.

The three fancy white diamonds showed moderate fluorescence peaks at the same wavelengths. One green and one gray-green (chameleon) diamond showed moderate-to-strong fluorescence intensities that were consistent with category 1.

Absorption Spectra. The UV-Vis-NIR spectra for three natural-color diamonds and three treated samples from the GIA collections with category 1 fluorescence showed the N3-related ZPL at 415 nm. The FTIR spectra of these diamonds, as well as four diamonds from the Aurora Butterfly collection, showed them to be type Ia, generally with both A and B aggregates in various concentrations. All three fancy white diamonds tested by FTIR spectroscopy showed significant concentrations of hydrogen, as evidenced by the 3107 cm^{-1} peak.

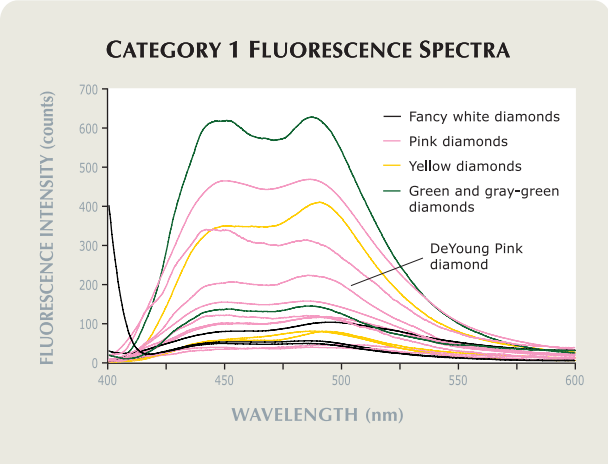
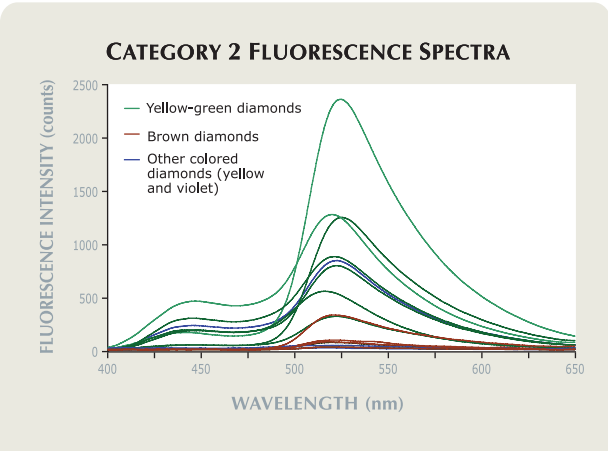


Figure 4. Category 1 fluorescence spectra (excited by 350 nm radiation) of natural-color diamonds with various bodycolors show similar peak positions and shapes due to the presence of the N3 defect.

Category 2: Fluorescence Spectra with a Dominant Peak at ~525 nm. Figure 5 shows a compilation of 350 nm–excited fluorescence spectra for the seven diamonds in the yellow-green group, six brown, and two other natural-color diamonds (violet and yel-

Figure 5. Category 2 fluorescence spectra (excited by 350 nm radiation) of natural-color diamonds with various bodycolors show similar peak locations and shapes. The responsible mechanism is the presence of H3 centers.



BOX B: PHOSPHORESCENCE SPECTROSCOPY OF NATURAL-COLOR DIAMONDS

Phosphorescence is quite rare in natural near-colorless diamonds, and its presence has been used to indicate a synthetic origin, as many such gems grown at high pressures and temperatures display some phosphorescence (Shigley et al., 2002). In our study, however, we recorded measurable phosphorescence on 56 of the 94 natural-color diamonds examined (see *G&G* Data Depository), with an intensity ranging from very weak to moderate, except for a few colors such as gray-green and blue that phosphoresce quite strongly (again, see Eaton-Magana et al., 2008). None of the irradiated diamonds we tested showed measurable phosphorescence. In our samples, there was a larger variety of peak shapes and positions in the phosphorescence than fluorescence spectra across all bodycolors, but general consistency within most bodycolors. Diamonds showing phosphorescence that is strong or that appears anomalous from the spectra obtained for natural stones may be suspect. Some diamonds showing strong phosphorescence (i.e., gray-green [most of which were chameleon] stones) are discussed in detail below, and the remaining bodycolors will be briefly summarized.

The empirical boundaries employed for describing phosphorescence spectra were: *very weak*, less than 5 counts; *weak*, 5–20 counts; *moderate*, 20–100 counts; *strong*, 100–300 counts; and *very strong*, >300 counts. When recording phosphorescence spectra, we evaluated its half-life instead of its duration. *Half-life* is defined as the time necessary for the initial intensity to decrease by one-half (see Watanabe et al., 1997). The more common term in gemology, *duration*, may be appropriate for visual observations, but it is actually a combination of two independent variables: initial intensity and the rate of decay. With phosphorescence spectroscopy, we are able to separate these variables to better distinguish one diamond from another. Additionally, the observed duration may be influenced not only by initial intensity, but also by the size of the stone. Therefore, *half-life* is preferable as it provides a better measure of the differences between the rates of phosphorescence decay because it is not influenced by these other factors. The longer the half-life is, the slower the rate of phosphorescence decay will be. Additionally, the shape of the decay curve (i.e., the rate at which intensity decreases with time) can indicate the mechanism causing the phosphorescence (again, see Watanabe et al., 1997).

Within most of the color groups, there were wide variations in calculated half-lives, with values between 0.2 and 4.8 seconds (for comparison, the half-life of the Hope Diamond is 8.2 seconds and the longest half-life we measured was 25.2 seconds [B234]).

The pink diamonds phosphoresced at weak-to-moderate intensity in a variety of wavelengths (half-life: 0.2–4.8 seconds). Two of the four yellow diamonds showed very weak phosphorescence centered at ~600 nm (half-life: 1.3–3.5 seconds); the other two did not show measurable phosphorescence. The three fancy white diamonds phosphoresced at moderate-to-strong intensity at ~450 and ~490 nm, identical to their fluorescence (half-life: 1.2–2.1 seconds). Six of 10 diamonds in the yellow-green group phosphoresced; they generally showed weak phosphorescence at 570–585 nm (half-life: 1.7–4.7 seconds). Seven violet and three type Ia blue-gray diamonds had weak-to-moderate phosphorescence at 565 nm (half-life: 0.25–4.2 seconds), and 4 of the 11 orange diamonds showed weak phosphorescence at a variety of wavelengths. None of the brown diamonds showed phosphorescence.

Therefore, while pink and orange diamonds showed a variety of phosphorescence patterns within their bodycolor range, we observed consistency within the color range for the other diamonds tested. Of particular interest were the gray-green (including chameleon) diamonds.

All eight gray-green (including chameleon) diamonds in the Aurora Butterfly collection and the four tested at GIA exhibited moderate phosphorescence

low) that showed distinctive asymmetry: a strong onset of fluorescence at ~500 nm, a peak maximum at ~525 nm (±7 nm), and a long tail on the high-wavelength side. Most of the spectra in figure 5 also showed a secondary peak at ~450 nm.

The yellow-green diamonds predominantly showed weak-to-moderate fluorescence intensity at ~445 nm and very strong asymmetric fluorescence centered at ~525 nm. Figure 6 shows fluorescence spectra at different excitation wavelengths for a green-yellow diamond that is representative of all seven diamonds of this color range.

The six brown diamonds showed weak-to-moderate fluorescence spectra with peaks centered at 510–532 nm. Figure 7 shows fluorescence spectra for one sample (GIA 12172-5b) obtained from the spec-

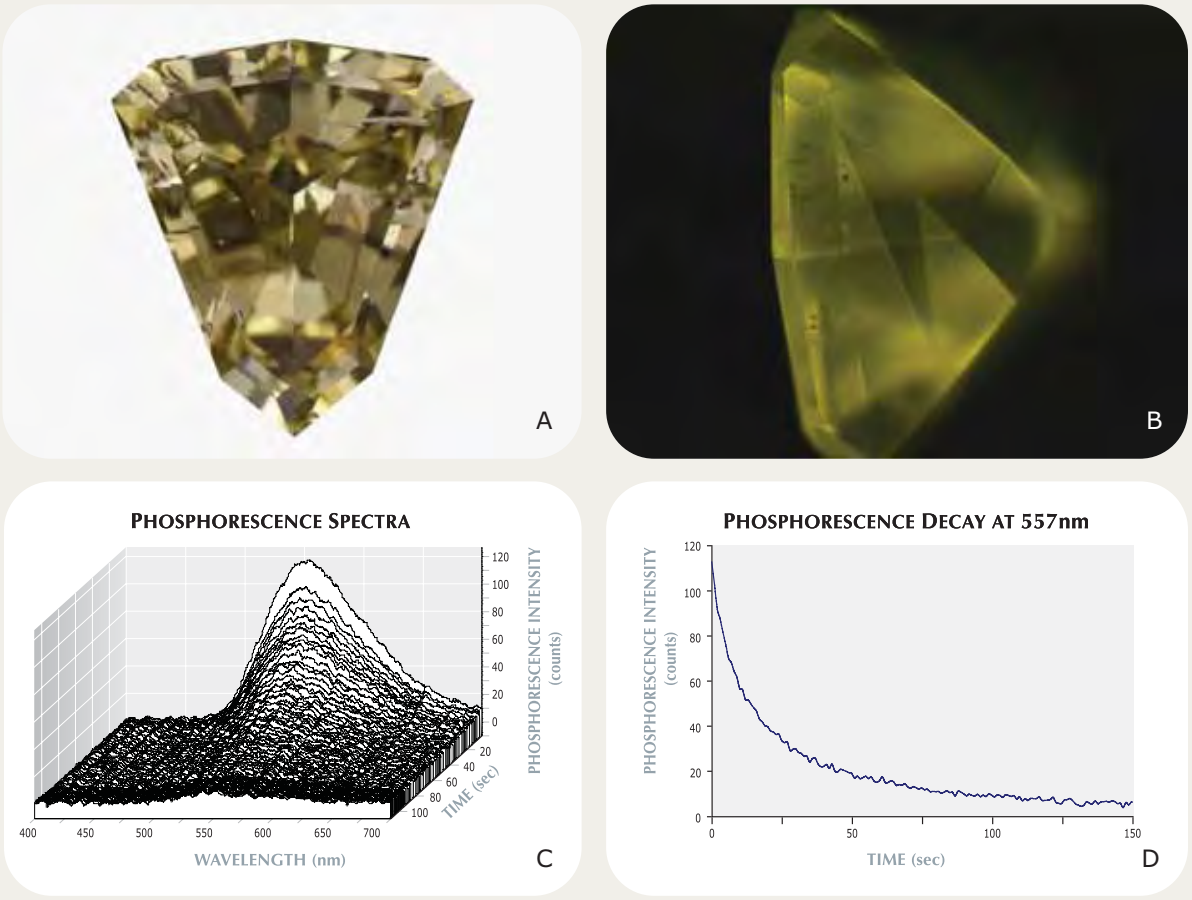


Figure B-1. Sample B231, a 0.79 ct chameleon diamond (A), shows greenish yellow phosphorescence in the DiamondView (B). Its phosphorescence spectra illustrate the decay of the diamond's phosphorescence with time (C). The phosphorescence spectrum at the back of the three-dimensional plot was taken immediately after the UV lamp was extinguished. The decay in intensity of the peak maximum (557 nm) with time is also provided (D). The calculated half-life is 13 seconds. Photos by Jian Xin (Jae) Liao (A) and S. Eaton-Magaña (B).

with peaks at 557–562 nm. These diamonds showed the greatest consistency in peak position of any of the color groups, and greater consistency in their phosphorescence than fluorescence spectra. The half-lives were long, ranging from 3.4 to 25.2 seconds. These samples had a similar rate of decay as that described by Watanabe et al. (1997) for synthetic type IIb diamonds. Figure B-1 shows a typical phosphorescence peak for the gray-green (chameleon) diamonds, and a corresponding plot of the decay of the phosphorescence maximum at 557 nm. Additional research is necessary to fully characterize the phosphorescence mechanism in these diamonds and to explain the variability in the measured half-lives.

trofluorometer compared to spectra obtained from the CCD spectrometer. The spectrofluorometer data show ZPLs for the N3 and H3 centers at 415 and 503 nm, respectively, along with their related sidebands. Due to the lower resolution of the CCD spectrometer, only the sidebands are observed in figure 7 (right).

A yellow diamond had a weak fluorescence spectrum, and a violet diamond showed a moderate fluorescence spectrum. Four irradiated diamonds also showed category 2 fluorescence: weak spectra were measured for the brownish orangy yellow and bluish green samples, and strong to very strong spectra were obtained from the greenish yellow samples.

Absorption Spectra. UV-Vis-NIR absorption spectra were collected for four natural and three treated

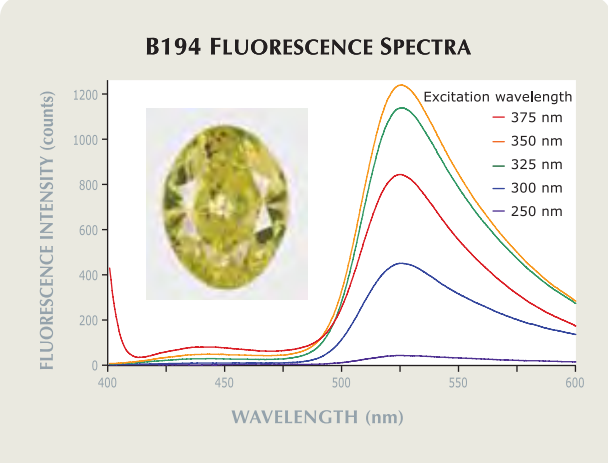


Figure 6. The fluorescence spectra of sample B194, a 0.51 ct green-yellow diamond, show a dominant peak at ~525 nm (i.e., category 2 fluorescence). The most intense fluorescence occurs when the stone is excited by UV radiation at ~350 nm. Photo by Jian Xin (Jae) Liao.

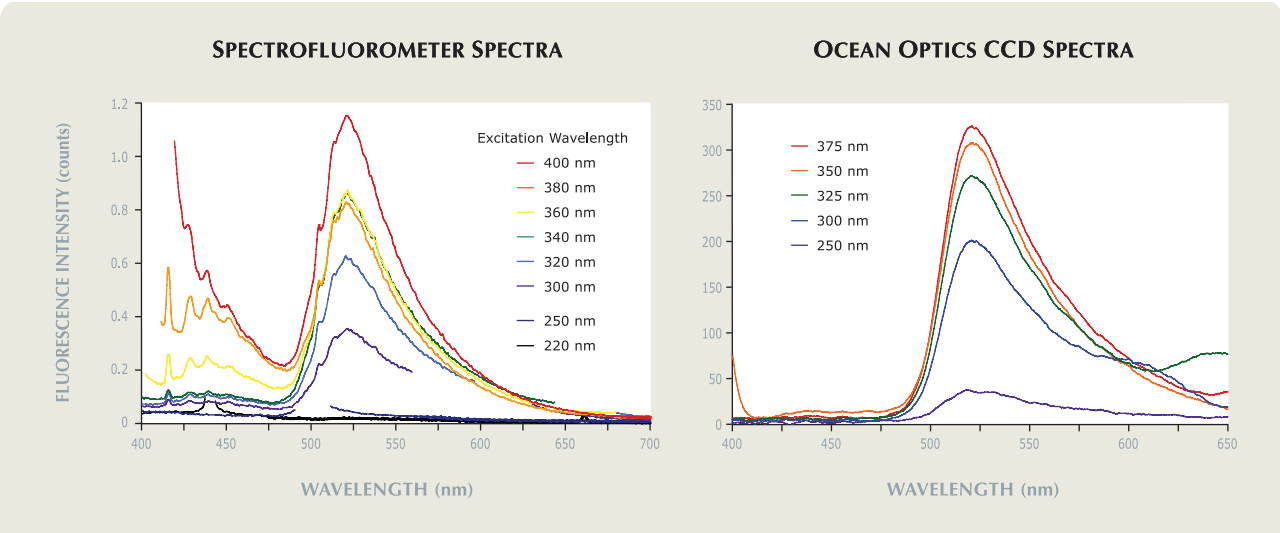
diamonds from the GIA collections that had category 2 fluorescence spectra (again, see table 1). All UV-Vis-NIR spectra showed the H3-related ZPL at ~504 nm. This peak was only observed in diamonds showing the category 2 fluorescence spectra. FTIR spectra of these diamonds along with an additional treated diamond showed they were type Ia, generally with both A and B aggregates in variable amounts.

Category 3: Fluorescence Spectra with a Dominant Peak at ~550 nm. Figure 8 shows a compilation of the category 3 fluorescence spectra, excited by 350 nm UV radiation, obtained from orange, violet, gray-green (including chameleon), and the type Ia diamonds in the blue-gray group.

One violet diamond along with three diamonds in the blue-gray group had fluorescence spectra with weak-to-moderate intensity at 525–530 nm. In a related study, 93% of the 67 gray-to-blue diamonds tested did not show measurable fluorescence, but showed phosphorescence spectra that proved to be distinctive of type IIb diamonds (Eaton-Magaña et al., 2008).

Most of the gray-green (including chameleon) diamonds indicated weak fluorescence at ~450 nm and moderate-to-strong fluorescence extending from ~450 to ~650 nm, with the center of the band ranging from 535 to 558 nm. Data obtained for a gray-green diamond using a spectrofluorometer at excitation wavelengths from 220 to 400 nm showed many interesting features (figure 9, left). The fluorescence intensity was quite low when excited at short UV wavelengths. However, as the excitation wavelength increased, the fluorescence intensity increased, with contributions from peaks centered at 495 and ~545 nm. The intensity reached a maximum when excited by UV radiation at 340–345 nm and then decreased as the wavelength of the excitation intensity increased further. At the higher excitation wave-

Figure 7. The graph on the left shows the fluorescence spectra for a 0.26 ct orangy brown diamond (GIA 12172-5b) collected at excitation wavelengths from 220 to 400 nm using the spectrofluorometer. Both N3- and H3-related luminescence may be observed, with ZPLs at 415 and 504 nm, respectively. The plot on the right shows the corresponding (lower resolution) fluorescence spectra obtained from the Ocean Optics CCD spectrometer.



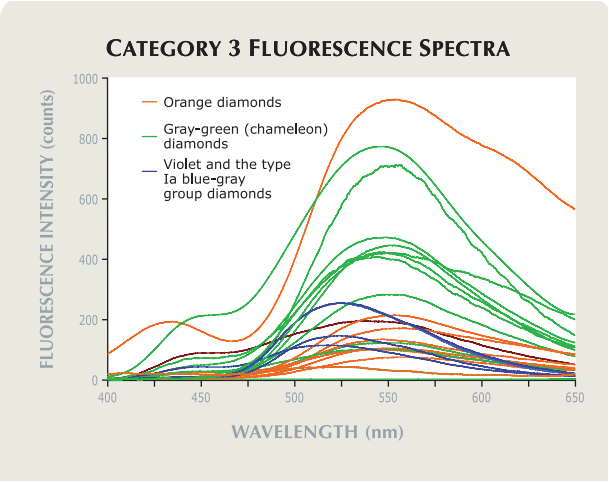


Figure 8. Category 3 fluorescence spectra (excited by 350 nm radiation) of the orange, violet, gray-green (including chameleon), and type Ia blue-gray diamonds have similar peak locations and shapes.

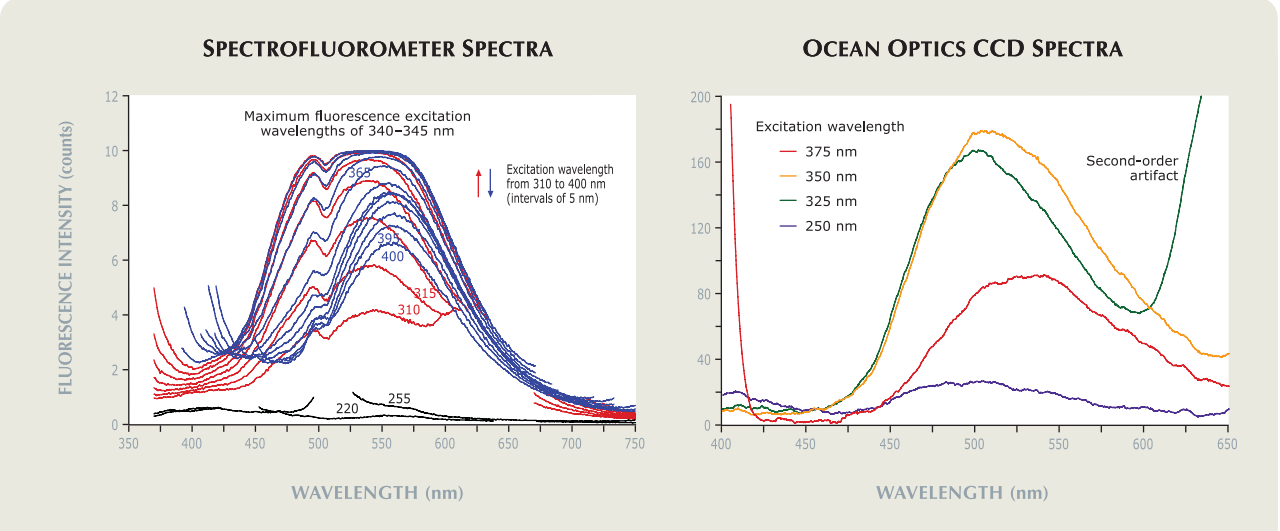
lengths, the two fluorescence peaks were centered at 495 and ~560 nm. The greater resolution of this instrument compared to the CCD spectrometer (figure 9, right) revealed the additional peak at 495 nm.

Of the 10 orange diamonds measured by fluorescence spectroscopy, seven showed weak-to-moderate and one showed strong category 3 fluorescence spectra with peaks ranging from 540 to 560 nm. Several of the diamonds also showed subordinate peaks at ~450 nm. The spectra at different excitation wavelengths illustrated in figure 10 for a Fancy Vivid yellowish orange diamond are representative of the other samples.

Absorption Spectra. FTIR spectra were collected for all eight gray-green (including chameleon) diamonds from the Aurora Butterfly collection with category 3 fluorescence spectra (again, see table 1), and FTIR and UV-Vis-NIR spectra were collected for the five diamonds from the GIA collections showing this fluorescence pattern. The UV-Vis-NIR spectra for these diamonds showed prominent bands centered at ~370 and ~480 nm.

The FTIR spectra of three diamonds in the blue-gray group indicated that they are type Ia instead of type IIb. Most blue diamonds receive their color from boron and are designated type IIb (see Fritsch and Scarratt, 1992, for an explanation of diamond types). The nitrogen concentrations in the category 3 diamonds generally were much lower for both the A aggregate (up to 114 ppm) and B aggregate (up to 22 ppm) compared to diamonds from categories 1 and 2: up to 415 and 890 ppm, respectively, for the A aggregate and up to 700 and 270 ppm, respectively, for the B aggregate.

Figure 9. These fluorescence spectra of a 0.52 ct gray-green diamond (GIA 12172-8b) were collected at excitation wavelengths of 220–400 nm with a spectrofluorometer (left) and at wavelengths of 250–375 nm with an Ocean Optics CCD spectrometer (right). Spectrofluorometer second-order artifacts (i.e., peaks at twice the excitation wavelength) have been removed for clarity. Also shown, at left, are the fluorescence spectra excited by wavelengths equivalent to a short-wave UV lamp (255 nm) and the DiamondView (~220 nm). The higher-resolution spectrofluorometer revealed a peak at 495 nm that was not visible with the CCD spectrometer.



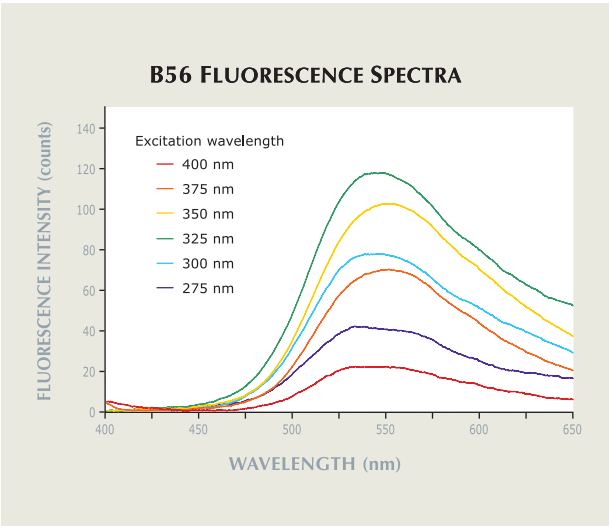


Figure 10. A 1.67 ct Fancy Vivid yellowish orange diamond, B56 (left), fluoresces moderate yellow-orange (center) with a long-wave UV lamp. The fluorescence spectra show a dominant peak at ~550 nm (i.e., category 3 fluorescence, right). The most intense fluorescence was recorded when excited by UV radiation at 325 nm. Photos by Jian Xin (Jae) Liao.

The orange, type Ia blue-gray group, and gray-green (including chameleon) diamonds that exhibited category 3 fluorescence spectra and were tested by FTIR spectroscopy all showed significant concentrations of hydrogen, as evidenced by the 3107 cm^{-1} peak.

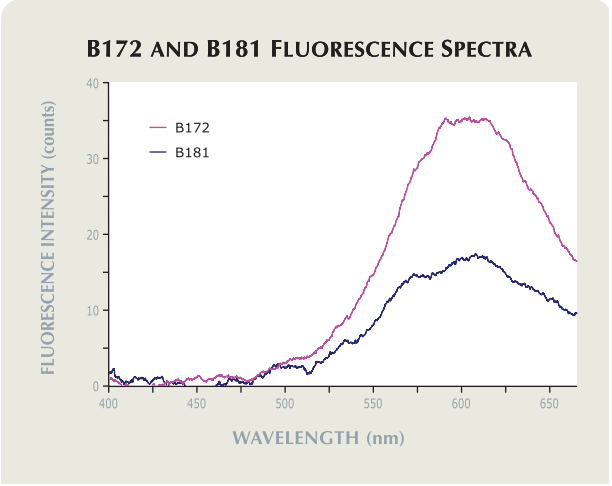
Natural Diamonds with Other Fluorescence Behavior. Two yellow-orange natural-color diamonds (172 and 181) showed fluorescence spectra (figure 11) with a single dominant peak at ~610 nm.

The one red and two purple diamonds were inert or did not show measurable fluorescence spectra. Admittedly, the number of samples we examined was small, but these colors are among the rarest of all natural diamonds. In the DeYoung Red, we observed a barely discernible yellow fluorescence to long-wave UV (inert to short-wave), which was noted also by Shigley and Fritsch (1993), who further documented a green luminescence when excited by 425 nm light. However, we could not discern a fluorescence spectrum with the CCD instrument. In the ultra-short-wave UV wavelengths of the DiamondView, the DeYoung Red showed blue fluorescence and well-defined growth bands, as well as a few narrow green zones (figure 12).

Figure 13 provides a summary of the categories of fluorescence spectra collected for the natural-color diamonds we examined, organized by key bodycolor.

Gemological Observations. The observed colors and intensities of long-wave UV fluorescence are summarized in table 1. Note that the fluorescence spectra did not always correlate directly to the fluorescence color observed with a standard UV lamp. Some reasons for such discrepancies are detailed in the Discussion section. The short-wave fluorescence was weaker for all the natural-color diamonds, and some diamonds exhibited no apparent luminescence to either UV wavelength. While no significant inhomogeneity or turbidity in the fluorescence colors was noted, we did not look specifically for such characteristics. A few samples showed a different fluorescence color when examined by the DiamondView, which was probably due to the difference in the excitation wavelength and/or saturation of the CCD camera used in the DiamondView instrument.

Figure 11. The fluorescence spectra of these two natural-color diamonds (B172 and B181) differ from those in the three common categories, with broad peaks centered at ~610 nm.



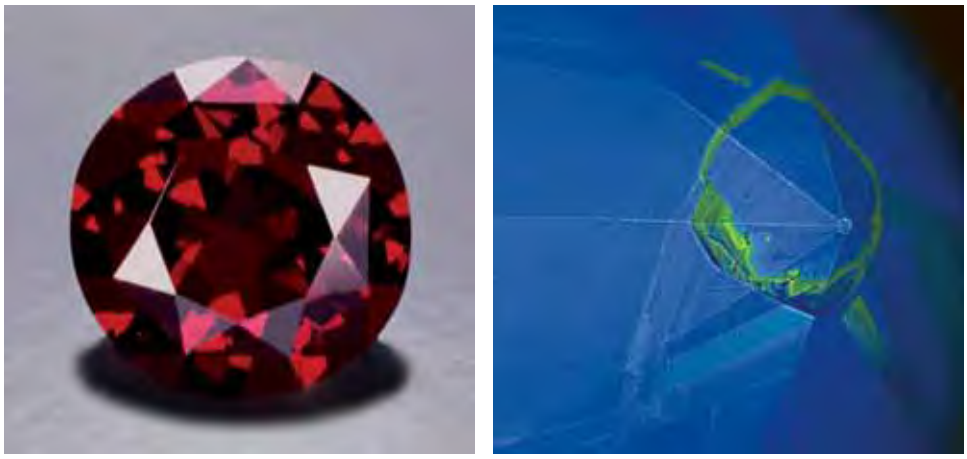


Figure 12. The DeYoung Red, at 5.03 ct, is one of the largest red diamonds in the world. Its DiamondView image shows a dominant blue fluorescence that is also typically observed in pink diamonds. Photos by Chip Clark (left) and S. Eaton-Magaña (right).

DISCUSSION

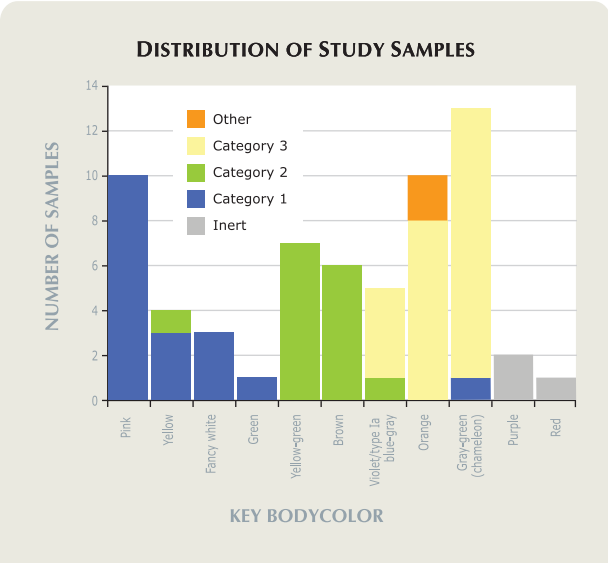
The vast majority of the fluorescence spectra for the natural-color diamonds tested fell into three categories with respect to the peak wavelengths and shapes. In fact, only two of the 62 natural-color diamonds described in this article (again, see figure 11) had peak positions other than those described in the three major categories (~450 and ~490 nm; ~525 nm; and ~550 nm). As shown in figure 13, the colored diamonds we tested are largely segregated into these three categories on the basis of their bodycolor. The information conveyed by these categories may provide clues to the origin of their color.

Category 1: Fluorescence Spectra with Dominant Peaks at ~450 and ~490 nm. For all the diamonds represented in figure 4, the fluorescence spectra show double peaks with maxima at ~450 (±12) nm and ~490 (±13) nm. This spectral pattern generally manifested itself as blue and is likely representative of fluorescence spectra for the vast majority of blue-fluorescing diamonds (e.g., Moses et al., 1997).

UV-Vis-NIR spectra of three natural and three irradiated diamonds showed the presence of the N3 center—a grouping of three nitrogen atoms in a (111) plane surrounding a vacancy—and higher-resolution spectra using the spectrofluorometer all confirmed that the ~450 and ~490 nm fluorescence peaks in the blue region of the spectrum are derived from the N3 center. The band centered at ~490 nm is artificially high in intensity, which is an artifact of the CCD spectrometer. On a spectrum for one sample obtained with the CCD spectrometer, radiometric correction of the output intensity across the wavelength range decreased the intensity of the ~490 nm peak so that it conformed better with spectra obtained from higher-resolution spectrofluorometers, thus confirming that the two observed peaks originate from the N3 center.

The category 1–fluorescing diamonds derive their bodycolors from different origins. Pink diamonds have a broad absorption band with a peak at 550 nm, which is thought to be due to plastic deformation (Fritsch, 1998). The color of most yellow diamonds is attributed to the N3 center, although some are colored by isolated nitrogen atoms (Fritsch, 1998). Fancy white diamonds are typically colored by light scattered from minute particles, some of which may be carbonates (Titkov et al., 2006), or their color may be related to the nitrogen B aggregate (Fritsch, 1998). Despite their different origins of color, all showed similar fluorescence spec-

Figure 13. Most of the 62 natural-color diamonds tested showed one of three distinct fluorescence spectra. Three diamonds included in this study were inert and two shared a different type of fluorescence spectrum.



tra, indicating a common tie among them, namely the presence of the common N3 center and the lack of more dominant fluorescing defects or significant concentrations of defects that can quench fluorescence, such as the A aggregate (Davies and Crossfield, 1973; Davies et al., 1974).

The category 1 fluorescence spectrum is associated with the N3 center, as is the subordinate peak at ~450 nm in the categories 2 and 3 fluorescence spectra (i.e., figures 5 and 8). This feature was seen in most of the diamonds, both natural and treated color.

Category 2: Fluorescence Spectra with Dominant Peak at ~525 nm. The spectral pattern shown in figure 5 generally manifested itself as bluish green to yellowish green fluorescence and is likely representative of the vast majority of green-fluorescing diamonds (Fritsch and Waychunas, 1994). The category 2 spectra are nearly identical to cathodoluminescence and photoluminescence spectra of a diamond with H3 defects (Collins and Woods, 1982). All seven of the category 2 diamonds for which UV-Vis-NIR absorption spectra were recorded (see table 1) showed the H3 center at 504 nm, and higher-resolution spectra taken with the spectrofluorometer on two of these samples (e.g., figure 7) confirmed the presence of the H3 center.

The H3 center results when a vacancy is trapped at the nitrogen A aggregate (Collins, 1982a). To create an H3 center, the diamond must be exposed to radiation and heat. These conditions are known to occur naturally, and the H3 center has been observed in natural, untreated diamonds (De Weerdt and Van Royen, 2001), although the luminescence of the center is greatly increased after deliberate irradiation and annealing (Collins et al., 2000).

Although yellow-green and brown diamonds show similar fluorescence spectra, these bodycolors have different origins. The green component of diamond color typically results from radiation damage (Fritsch, 1998). However, this color appearance may also be caused by strong green luminescence (much like the Portuguese Diamond can appear bluish due to its blue fluorescence; Fryer and Koivula, 1986). The specific defect that causes the color of brown diamonds is unknown, but it is believed to be related to the plastic deformation mechanism that also causes pink coloration (Fritsch, 1998). Theoretical modeling has suggested that brown coloration may be related to large vacancy disks (Hounsome et al., 2006).

We observed an inverse correlation between the concentration of A aggregates and the intensity of the 525 nm peak (figure 14); therefore, the presence of A aggregates appears to quench H3-related luminescence. This observation was noted previously (Zaitsev, 2001), and such data confirm the usefulness of this spectrometer for a variety of applications.

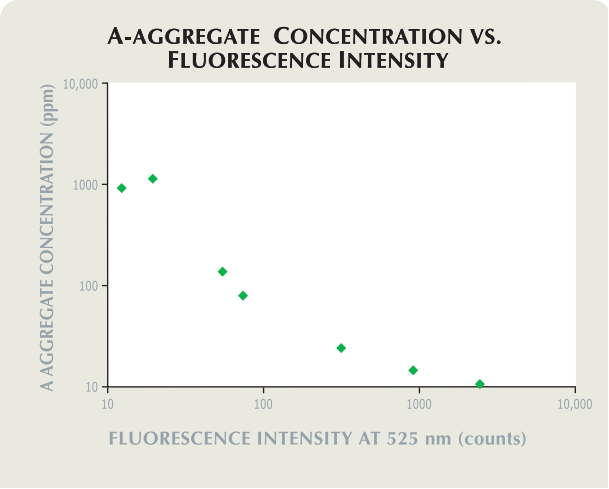


Figure 14. A comparison of the intensity of the green fluorescence at 525 nm with the concentration of A aggregates in each diamond (as calculated from the FTIR spectra) shows an inverse correlation. The fluorescence spectra were collected over 30 seconds, and both concentrations and intensities are presented here on logarithmic scales.

Category 3: Fluorescence Spectra with Dominant Peak at ~550 nm. All the diamonds represented in figure 8 showed similar fluorescence spectra. This spectral pattern generally manifested itself as yellow to orangy yellow fluorescence, and is likely representative of the fluorescence spectra for the vast majority of fluorescence observations within this color range (Fritsch and Waychunas, 1994).

Most of the spectra showed a broad (FWHM ~100 nm), rather symmetrical peak centered at 530–560 nm. They are similar to a fluorescence spectrum published for a 22 ct chameleon diamond (Fritsch et al., 1995), also excited by 350 nm radiation. Nearly all of the category 3 diamonds showed a secondary peak at ~450 nm that correlated to the N3 defect in those samples tested by UV-Vis-NIR spectroscopy. The absorption spectra also showed the presence of the 480 nm band in these diamonds. Previous researchers have observed yellow fluorescence in diamonds with a 480 nm band (Collins, 1980; Collins, 1982b; Hainschwang et al., 2005), or in those that are rich in hydrogen (Fritsch and Scarratt, 1992). The 480 nm band is a common feature in orange and chameleon diamonds (Hainschwang et

al., 2005); however, a great many issues about the origin of the 480 nm band are still unresolved.

The category 3 fluorescence spectra may be linked to the high concentration of hydrogen that was observed in chameleon, other gray-green, type Ia blue-gray, and orange diamonds by FTIR spectroscopy. Among the diamonds from other fluorescence categories that were tested by FTIR, only the fancy white diamonds had consistently measurable hydrogen-related peaks at 3107 cm^{-1}.

Although violet, type Ia blue-gray, gray-green (including chameleon), and orange diamonds may show similar fluorescence spectra, their bodycolors are derived from different origins. Hydrogen has been observed in violet and type Ia gray-to-blue diamonds (Robins et al., 1991; Fritsch and Scarratt, 1992; Fritsch and Scarratt, 1993), but the specific configuration causing the color has not yet been identified. The origin of orange color is unknown (Bosshart, 1999), but it most likely derives from nitrogen-related defects (Fritsch, 1998). The color of gray-green and chameleon diamonds has been linked to the presence of a rare nitrogen-related defect that gives rise to the 480 nm band along with hydrogen centers (Massi et al., 2006).

None of the 10 treated diamonds showed category 3 fluorescence spectra, but study of a broader group of such diamonds is needed to confirm this trend.

Fluorescence Spectra with Dominant Peak at ~610 nm. Two yellow-orange diamonds showed broadband fluorescence with peaks centered at ~610 nm (again, see figure 11). This spectral pattern, which is very different from those described above, would generally manifest itself as brownish orange fluorescence. We were unable to positively identify the defect responsible, but it is likely related to the neutral N-V center with its ZPL at 575 nm (Anderson, 1960, 1962; Martineau et al., 2004). In sample B181, a slight peak at ~575 nm is suggestive of this mechanism as well.

Comparison to Observed Fluorescence. The color of observed fluorescence is typically recorded as a response to long- or short-wave UV radiation. In actuality, many UV lamps do not provide single, isolated peak emissions at 365 nm for long wave and at 254 nm for short wave (Williams, 2007). Instead, long-wave lamps often contain peaks at 404 and 435 nm, in addition to a broad band that extends from the UV into the visible region of the spectrum; likewise, many short-wave lamps show peaks at 315 and 365 nm (i.e., long-wave UV; again, see Williams [2007] for more information). This was the case for the gemological UV lamps used in this study. Therefore, the fluorescence observed using most gemological lamps is a combination of fluorescence excited by several wavelengths and, in the case of long-wave UV, by the influence of light in the visible region (S. Elen, pers. comm., 2007). A stone that is believed to show "weak fluorescence" to short-wave UV may actually be responding to the long-wave component present in the lamp. It is not surprising, then, that the observed color of fluorescence taken with standard long- and short-wave UV lamps may not be directly analogous to the results presented here. The spectra recorded by the fluorescence spectrometer are activated by a narrow range of wavelengths that do not include radiation at other wavelengths and do not extend into the visible range.

While examining the DeYoung Red, we observed a very weak yellow fluorescence using a long-wave UV lamp, but we could not resolve a fluorescence spectrum with the CCD spectrometer. There could be several explanations for this discrepancy. The sensitivity of the instrument may have been too low to detect the yellow fluorescence, while the relatively large size of the DeYoung Red (5.03 ct) aided the visual observation of this luminescence. Alternatively, Shigley and Fritsch (1993) noticed a green luminescence when the diamond was excited at 425 nm. The observed yellow fluorescence when exposed to the long-wave UV lamp could be due to excitation outside the narrow band of UV radiation used in our spectroscopy experiments.

As mentioned above, the additive effect of fluorescence to the eye due to a gemstone's size is also a factor. The Portuguese diamond (figure 15) is famous for its strong blue fluorescence, which can be seen easily in ambient light. However, as the spectra in figure 15 show, the intensity of its fluorescence spectrum is not extraordinarily high relative to those of other diamonds. The combined effect of its large size (127.01 ct) with its fluorescence is what makes this diamond so notable.

In addition to the ambiguity of the excitation wavelength of UV lamps, the interpretation of fluorescence color can be difficult as well. Due to the contribution of subordinate peaks and the length of the tail of a fluorescing band, diamonds with fluorescence emissions of similar origin can yield fluorescence colors that are quite different. Figure 16 shows the effect of a subordinate peak in the diamond fluorescence spectra, and figure 17 shows the effect of a long spectral tail. As demonstrated by

Figure 15. The 127.01 ct very slightly yellow (G-to-I on the GIA color-grading scale) Portuguese diamond (left) is famous for its strong blue fluorescence (center). Yet its fluorescence spectrum (right) reveals that the intensity measured from a limited volume is comparable to that of smaller fancy-colored yellow diamonds that also show category 1 fluorescence. Photos by Chip Clark.

these examples, slight differences in peak positions and shapes may lead to considerable variation in the literature regarding reported fluorescence colors, even if the underlying causes of the luminescence are identical. Furthermore, gemologists could misinterpret the observed fluorescence of two diamonds that appear to fluoresce with similar colors as an indication that they have similar properties. For example, a comparison of observed fluorescence for diamond 1 in figure 16 against diamond 3 in figure 17 shows that both appear as shades of green. However, examination of the corresponding spectra indicates that the defects causing the observed fluorescence appear to be quite different.

Analysis of the Spectrometer. The absolute intensities of fluorescence measured in the spectra will, of course, depend on the UV radiation source. Within this study, we maintained a consistent measurement technique and geometry when using the CCD spectrometer, and we believe that the measured intensities are comparable between these diamonds. Our results were sufficiently consistent that we feel our spectroscopy system (i.e., figure 2; see box A for more information) allows semiquantitative intensity assignments based on the measured counts to replace the visual assessment descriptions that typically are used to describe diamond fluorescence, such as *weak*, *moderate*, and *strong*.

Implications for the Gemologist. Observed fluorescence is often included with the other properties of a diamond. However, the reliability of such data is called into question by the many ambiguities inherent in these observations, such as the viewer's estimation of intensity and color, the effect of the size of the sample, and the actual wavelengths of UV excitation. Here, we investigated the information provided by fluorescence spectroscopy on a wide variety of colored diamonds. Although there are large variations in the fluorescence colors reported for diamond (again, see, Fritsch and Waychunas, 1994), fluorescence spectroscopy was able to distill that variety into three main spectral patterns by discerning the contribution of subordinate peaks and long tails. Although this work was performed exclusively on colored diamonds, we are confident that valuable information could be gained on other gem materials as well.

As stated earlier, diamonds with fluorescence spectra that appear anomalous to the three main categories may be considered suspect. Additionally, the irradiated stones in table 1 indicate that samples with fluorescence spectra that appear similar to these three categories but do not conform to one of the bodycolor designations may be treated. However, with some colored diamonds, such as those with yellow-green bodycolors, fluorescence spectroscopy may not be a reliable indicator of treatment.

Fluorescence and phosphorescence spectra have a number of other potential applications as well. They could help explain unusual fluorescence and phosphorescence, such as the type IIb diamond with multiple colors of phosphorescence reported by Moe and Johnson (2007). Phosphorescence spectroscopy can distinguish between type Ia gray-to-blue diamonds and type IIb blue diamonds (see box B and Eaton-Magaña et al., 2008). In fact, the phosphorescence spectra of type IIb blue diamonds proved so distinctive of each diamond that the researchers termed it a "fingerprint" that could individually classify a type IIb diamond (again, see Eaton-Magaña et al., 2008).

Fluorescence spectroscopy can also help the gemologist distinguish between natural and synthetic diamonds. Martineau et al. (2004) correlated

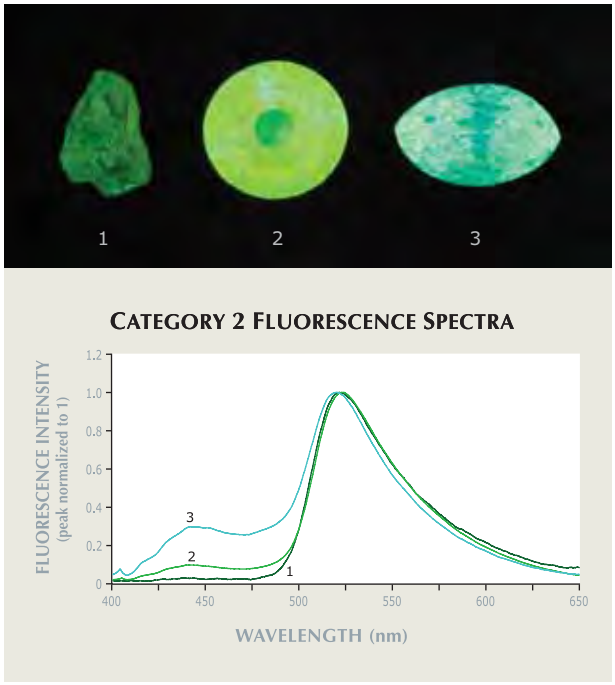


Figure 16. All of these diamonds (GIA 12172-5b [1], GIA 22020 [2], and GIA 21542 [3]) show category 2 fluorescence spectra, with a dominant peak at ~525 nm caused by the H3 defect. However, slight differences in peak shape and the presence of an N3-related subordinate peak centered at ~450 nm cause the observed fluorescence colors to appear different. The fluorescence photo was excited by narrow-band 365 nm radiation (also used to collect the spectra), and not a standard long-wave UV lamp. Photo by Shane Elen.

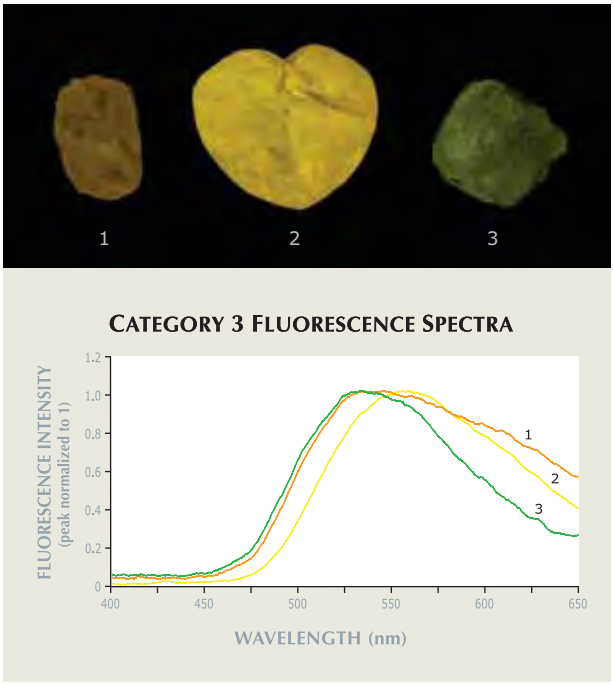


Figure 17. All of these diamonds (GIA 12172-8b [1], GIA 487988302 [2], and GIA 12172-8a [3]) show category 3 fluorescence spectra that are likely related to the 480 nm absorption band. Variations in peak position and shape cause the observed fluorescence colors to appear quite different. The fluorescence photo was excited by the same narrow-band 365 nm radiation that was used to collect the spectra. Photo by Shane Elen.

orange fluorescence observed in chemical vapor deposition (CVD) synthetic diamonds with the 575 and 637 nm lines seen in their photoluminescence spectra; Wang et al. (2005) made similar observations on treated pink-to-red diamonds. While visual assessment of fluorescence would be unable to reliably distinguish between the orange fluorescence sometimes observed in category 3 natural diamonds and the 575 nm–induced fluorescence observed in synthetic diamonds, treated-color diamonds, and some rare natural-color diamonds, spectroscopy could help make the distinction.

Other gemological testing equipment, such as the DiamondSure, looks for the presence of the N3 center in natural diamonds to help distinguish them from near-colorless synthetics (Welbourn et al., 1996). The N3-related center cannot be reliably confirmed by the mere observation of blue fluorescence; however, its presence in a fluorescence spectrum is a strong indicator that a diamond has a natural origin.

A laboratory might also offer more complete comparisons of long- and short-wave fluorescence (e.g., that the intensity of the short-wave fluorescence was 30% that of the long-wave fluorescence). This information would contribute to a more thorough characterization of the diamond for identification purposes.

While the equipment used in this study will not replace laser-excited spectrometers (such as FTIR or Raman) or higher-resolution spectrofluorometers used in gemological research laboratories, the affordability of the CCD spectrometer used in these tests makes it available to a greater number of gemologists. Its speed and ease of use make it possible to quickly and conveniently characterize large numbers of stones.

CONCLUSIONS

This work reports the fluorescence properties of 62 natural-color diamonds that span nearly the entire color spectrum observed in natural diamonds. For comparison, the spectra of 10 irradiated diamonds were also measured.

Due to limitations on the number of colors and kinds of diamonds used in this study, the fluores-

Figure 18. Fluorescence spectroscopy can help characterize important diamonds such as these 0.51–2.03 ct stones from the October 2007 Argyle tender. Highlights of the tender included the 1.74 ct Fancy purplish red oval, the 0.69 ct Fancy purplish red emerald cut, and the 0.77 ct Fancy Dark gray-violet shield shown here. Courtesy of Argyle Diamond; photo by Robert Weldon.

cence spectra reported here likely do not represent the entirety of possible fluorescence behaviors in natural or treated diamonds. For example, we did not test all known types of treated diamonds. Diamonds with different fluorescence spectra from those documented in this article could have additional color centers or combinations of centers. Nevertheless, this work illustrates the potential of this relatively inexpensive equipment, the mobile CCD spectrometer, for a more precise characterization of the fluorescence and phosphorescence properties of diamonds, especially important ones (figure 18). Our experience suggests that the attributes of this instrument make it suitable for rapidly characterizing the luminescence properties of large numbers of diamonds and other gems. Fluorescence spectra yield far more information than visual assessment alone, such as a semiquantitative assessment of intensity and the presence of subordinate peaks, and are much less ambiguous.

The vast majority of the fluorescence spectra fell into three major categories with respect to peak wavelengths and shapes. Only two of the 62 natural-color diamonds had peak positions other than those described in the three major categories. The fluorescence spectra were largely segregated by the diamonds' bodycolors. Category 1 fluorescence spectra were predominantly represented by pink, yellow, and fancy white natural-color diamonds; category 2 by natural diamonds in the yellow-green group or with brown bodycolors; and category 3 by natural diamonds with orange or gray-green (including chameleon) bodycolors or in the type Ia blue-gray group of natural diamonds. Evidence of an anomalous fluorescence spectrum may indicate that a stone needs to be submitted for additional testing.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the considerable contribution of Alan Bronstein and Harry Rodman for the loan of their Aurora collections. Thomas Moses, Dr. Wuyi Wang, and Kyaw Soe Moe, of the GIA Laboratory in New York, graciously loaned the DiamondView instrument, performed FTIR measurements, and collected color grading and origin-of-color information on some diamonds in the Aurora Butterfly collection. At the GIA Laboratory in Carlsbad, Shane Elen provided help and advice in operating the spectrofluorometer, and Karen Chadwick helped collect FTIR and UV-Vis-NIR data. Russell Feather helped with obtaining some of the data at the Smithsonian Institution. Financial support was provided by the Office of Naval Research and the Naval Research Laboratory. This research was partially funded by a National Research Council Fellowship Award to Dr. Eaton-Magaña.

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