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# THE SEPARATION OF NATURAL FROM SYNTHETIC COLORLESS SAPPHIRE

By Shane Elen and Emmanuel Fritsch

*Greater amounts of colorless sapphire—promoted primarily as diamond substitutes, but also as natural gemstones—have been seen in the gem market during the past decade. In the absence of inclusions or readily identifiable growth structures, natural colorless sapphires can be separated from their synthetic counterparts by their trace-element composition and short-wave ultraviolet (SWUV) transparency. Energy-dispersive X-ray fluorescence (EDXRF) analysis shows higher concentrations of trace elements (i.e., Fe, Ti, Ca, and Ga) in natural sapphires. These impurities cause a reduction in SWUV transparency that can be detected by UV-visible spectrophotometry (i.e., a total absorption in the UV region below 280–300 nm, which is not seen in their synthetic counterparts). This article describes a SWUV transparency tester that can rapidly identify parcels of colorless sapphires.*

## ABOUT THE AUTHORS

Mr. Elen ([selen@gia.edu](mailto:selen@gia.edu)) is a research gemologist at GIA Research, Carlsbad, California, and Dr. Fritsch is professor of physics at Nantes University, France.

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Hundreds of millions of carats of colorless synthetic sapphire are manufactured annually (all growth techniques combined), according to B. Mudry of Djvahirdjian in Monthey, Switzerland, a leading producer of Verneuil synthetics (pers. comm., 1997). He estimates that about 5%–10% of this production (50–100 million carats) is used by the jewelry industry. Distinguishing natural from synthetic colorless sapphire can often, but not always, be accomplished by standard gemological testing (see below). However, this distinction is time consuming for large parcels, and it is difficult to impossible for melee-size stones.

As first described more than 50 years ago (Wild and Biegel, 1947), natural colorless corundum can be separated from flame-fusion synthetic colorless corundum (only Verneuil material was being produced at that time) by a difference in transparency to short-wave ultraviolet (SWUV) radiation. The present study shows that the difference in SWUV transparency is a result of the difference in trace-element chemistry between natural and synthetic colorless sapphire. We also demonstrate that SWUV transparency testing is valid for Czochralski-grown synthetic colorless sapphire, too. Therefore, this technique can help meet the need for a simple, cost-effective method to mass screen this relatively inexpensive gem material.

## BACKGROUND

**Natural Colorless Sapphire.** Colorless sapphire is a relatively pure form of aluminum oxide ( $\text{Al}_2\text{O}_3$ ); it is often inaccurately called “white sapphire.” Truly colorless sapphire is quite uncommon, and most “colorless” sapphire is actually near-colorless, with traces of gray, yellow, brown, or blue. For the purposes of this article, both colorless and near-colorless sapphires will be referred to as “colorless.” The primary source for this material has been, and remains, Sri Lanka.

Colorless sapphire was a common diamond simulant in

Figure 1. Colorless sapphire continues to be popular in jewelry, especially for items such as tennis bracelets, but also as single stones. The larger loose sapphire is 4.44 ct; the tennis bracelet contains a total weight of 4.33 ct; the stone in the pendant is 8.56 ct and the sapphire in the ring is 5.17 ct. Courtesy of Sapphire Gallery, Philipsburg, Montana; photo © Harold & Erica Van Pelt.



the late 19th and early 20th centuries. In the early 1970s, it first began to be used as an inexpensive starting material for blue diffusion-treated sapphires (Kane et al., 1990). At around the same time, large quantities of colorless sapphire were heat treated to produce yellow sapphire (Keller, 1982). The demand for colorless sapphire increased significantly in the late 1980s to early 1990s. This was a result of the greater interest in blue diffusion-treated sapphires (Koivula et al., 1992), and colorless sapphire's increasing popularity in jewelry as an affordable alternative to diamond that could be used as melee, for tennis bracelets, or attractively set as a center stone (Federman, 1994).

From 1993 through the first half of 1994, a steady demand for faceted colorless sapphire caused the per-carat price to almost double, to US\$70 per carat retail ("White sapphire sales up 172%," 1994). Colorless sapphire jewelry (figure 1) has remained

popular ("Demand strong for white sapphires," 1996; M. Schramm, pers. comm., 1999), and has fueled a market for synthetic colorless sapphire.

**Synthetic Colorless Sapphire.** Synthetic sapphire has been produced by several growth techniques—in particular, flux, hydrothermal, flame-fusion, and Czochralski. However, because of manufacturing costs, only two types of synthetic colorless sapphire are typically used as gems: flame-fusion (Verneuil, 1904) and Czochralski "pulled" (Rubin and Van Uitert, 1966). Early in the 20th century, flame-fusion synthetic colorless sapphire was the first synthetic gem material to be used as a diamond simulant (Nassau, 1980, p. 210). However, other synthetic gem materials have since surpassed colorless synthetic sapphire for this purpose because of the significantly lower refractive index and dispersion of corundum as compared to diamond.



Figure 2. These stones (0.32 ct to 3.08 ct) formed part of the sample set used in this study. The colorless sapphires on the left are synthetic, and those on the right are natural. Photo © Tino Hammid and GIA.

Early synthetic sapphire produced by the Verneuil method often contained characteristic growth defects, such as striations and inclusions. These defects were unacceptable to the industrial market, which required extremely high (“optical”) quality synthetic sapphire. This led to the development of several new growth techniques, including the Czochralski method, which provides the highest-quality single crystals for application in high-performance optics, sapphire semiconductor substrates, watches, and bearings (Nassau, 1980, p. 84). With these refinements, the characteristics that were previously used to separate natural from synthetic colorless sapphire became less obvious or were eliminated, and the separation became considerably more difficult.

**Review of Identification Techniques.** In many instances, larger natural and synthetic colorless sapphires (see, e.g., figure 2) can be separated by standard gemological methods, such as microscopy (for the identification of inclusions and the study of growth structures visible with immersion) or UV-induced fluorescence (see below). However, smaller,

melee-size sapphires may not exhibit any characteristic inclusions or growth structures. R.I. and S.G. values are of no help, as they are identical for synthetic and natural stones (Liddicoat, 1987, p. 338).

*Inclusions.* Natural colorless sapphire contains the same distinctive inclusions encountered in other color varieties of corundum: silk (fine, needle-like rutile or boehmite crystals), groups of rutile needles intersecting in three directions at 60° to one another, zircon crystals surrounded by stress fractures, and well-defined “fingerprint” inclusions (figure 3) that consist of large networks of irregular fluid-filled cavities (Gübelin, 1942a and b, 1943; Kane, 1990). Two- and three-phase inclusions may be encountered, as well as small crystals of spinel, uraninite, mica, pyrite, apatite, plagioclase, albite, and dolomite (Gübelin and Koivula, 1992; Schmetzer and Medenbach, 1988).

Colorless synthetic sapphire may exhibit growth-induced inclusions, typically small gas bubbles (figure 4) or unmelted aluminum oxide particles that occur individually, in strings, or in “clouds.” Gas bubbles may appear round or elongated in a flask or tadpole shape (figure 5). The gas bubbles may follow curved trajectories, allowing indirect observation of the curved striae that are otherwise invisible in colorless synthetic sapphire (Webster, 1994).

The irregularly shaped gas bubbles in synthetic corundum could be mistaken for natural crystal inclusions with partially dissolved crystal faces. Occasionally, undissolved alumina may take on the appearance of a natural inclusion (Webster, 1994). As noted above, however, recent production tech-

Figure 3. This “fingerprint” is actually a partially healed fracture that exhibits a network of fluid inclusions; it is typical of natural colorless sapphire. Photomicrograph by Shane Elen; magnified 20×.

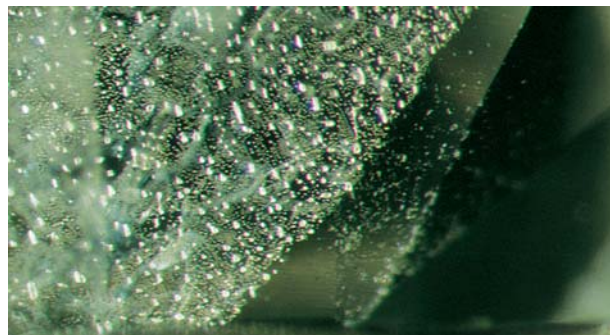




Figure 4. This group of gas bubbles is typical of Verneuil synthetic sapphire. Photomicrograph by Shane Elen; magnified 20 $\times$ .

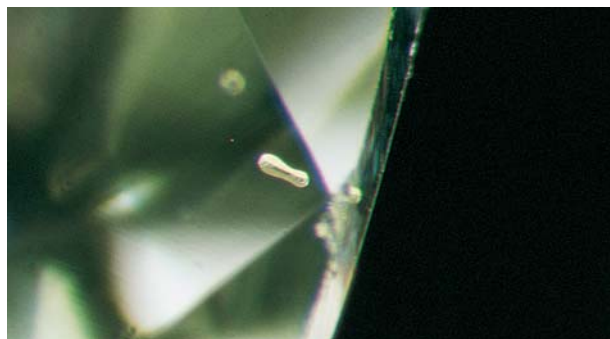


Figure 5. Although bubbles are uncommon in Czochralski-grown synthetic sapphires, this flask-shaped bubble was noted in one of the samples. Photomicrograph by Shane Elen; magnified 20 $\times$ .

niques have almost entirely eliminated any characteristic inclusions, especially in the case of Czochralski-grown synthetic corundum, which has a strictly controlled growth environment.

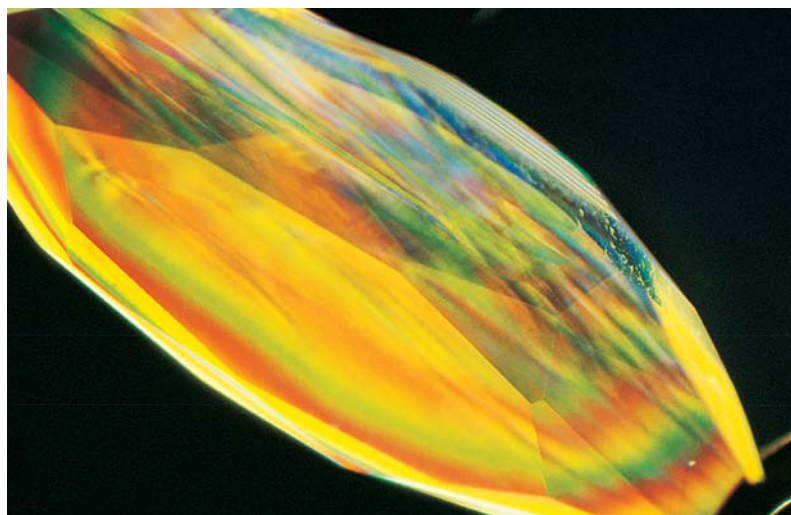
*Growth Structures.* Immersion microscopy often can reveal internal growth features such as twinning or growth planes in corundum (Smith, 1996). The detection of Plato lines (Plato, 1952; figure 6) may identify Verneuil synthetic sapphire, which does not always exhibit visible growth features. However, heat treatment of colorless flame-fusion synthetic sapphire can make growth structures even less apparent (Kammerling and Koivula, 1995), and we have never observed Plato lines in colorless synthetic sapphire grown by the Czochralski method. Furthermore, observation of growth structures by immersion microscopy is not easy, and requires some practice and understanding of crystallography.

*Other Techniques.* Energy-dispersive X-ray fluorescence (EDXRF) spectrometry has been used for the chemical analysis of many different gemstones (Stern and Hänni, 1982), most recently for the separation of natural from synthetic ruby (Muhlmeister et al., 1998). This semi-quantitative method used to identify trace elements is particularly suited for gemstones such as colorless sapphire that may not exhibit inclusions or growth features. However, the technique requires expensive equipment and a trained operator, and it can test only one stone at a time.

In addition, natural and synthetic colorless sapphires may exhibit different luminescence reactions to UV radiation, cathode rays (electron beam), and X-rays (Anderson, 1990; Webster, 1994). Some gemologists have used UV luminescence (figure 7)

as a first step in separating batches of natural and synthetic colorless sapphire: Stones that show chalky blue fluorescence to SWUV radiation are considered synthetic, but those that are inert could be either natural or synthetic, so they must be individually evaluated for other distinguishing characteristics (C. Carmona, pers. comm., 1999). However, because the intensity and color of the luminescence is not consistent within each group (i.e., natural or synthetic), luminescence is not a conclusive test. UV fluorescence or cathodoluminescence can be used for positive identification of colorless sapphire only when characteristic growth features—such as the angular growth zoning typical of natural stones

Figure 6. Plato lines may be observed in some Verneuil synthetic sapphire by viewing the sample (while it is immersed in methylene iodide) down the optic axis with cross-polarized light. Photomicrograph by Shane Elen; magnified 3 $\times$ .



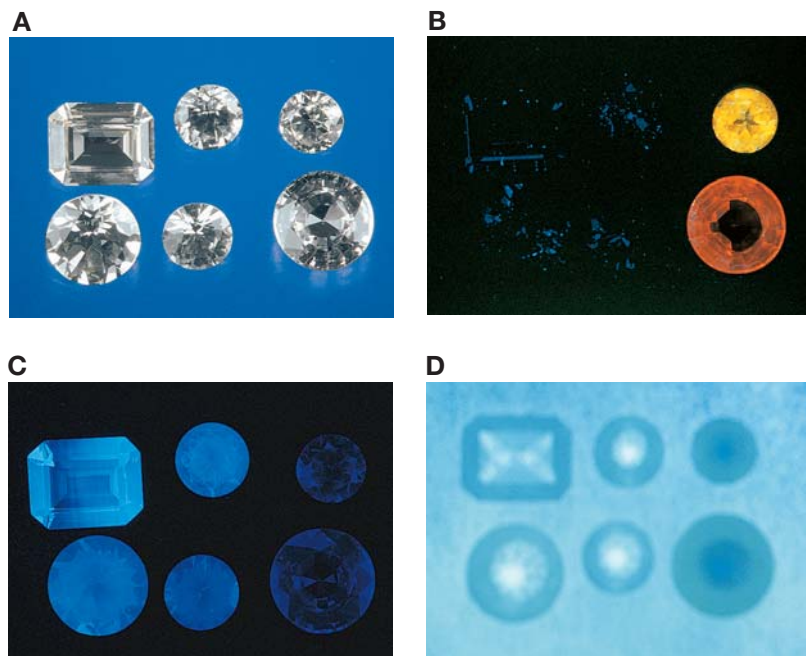


Figure 7. These six samples of natural (two on the far right) and synthetic (the Czochralski, the two in the middle; Verneuil, the two on the far left) sapphires range from 0.78 to 2.75 ct. They were photographed with: (A) natural light, (B) long-wave (LW) UV, (C) SWUV, and (D) in the SWUV transparency tester. Here, the synthetic samples are inert to LWUV, while the natural stones fluoresce strongly yellow and orange; all the synthetics fluoresce chalky blue to SWUV, but the natural stones are inert (the slight blue is due to reflection from the synthetics). Although these fluorescence colors are typical, they are not consistent. The natural sapphires appear dark in the SWUV transparency tester because they absorb SWUV; the synthetic sapphires appear transparent. Photo A by Maha DeMaggio; B–D by Shane Elen.

(figure 8) and the curved striae seen in synthetic sapphires (figure 9)—are observed in the luminescence patterns (Ponahlo, 1995; Kammerling et al., 1994). However, these features may be difficult to resolve, and magnification is frequently required.

More than 50 years ago, Wild and Biegel (1947) noted that natural and synthetic (Verneuil) colorless sapphires differed in their transparency to short-wave UV radiation (again, see figure 7). Colorless synthetic corundum subsequently was found to exhibit transparency down to 224 nm, whereas colorless natural corundum did not transmit below 288 nm (Anderson and Payne, 1948). Theoretically, pure corundum is extremely transparent to short-wave UV because of its lack of impurities, and should exhibit transparency down to 141 nm (French, 1990). As the level of impurities increases, the transparency to SWUV decreases. Although transparency to SWUV may be decreased in stones that are heavily flawed, the colorless sapphire in the jewelry market is typically “eye clean.”

Yu and Healey (1980) applied these SWUV transparency differences to the separation of natural from synthetic *colored* corundum by means of an instrument called a *phosphoroscope* (Yu and Healey, 1980). Its use for this purpose was limited, though, because colored synthetic corundum grown by the hydrothermal and flux methods often exhibited SWUV absorption similar to that of natural corundum of comparable color. However, hydrothermal

and flux synthetic sapphires are not commercially available in colorless form, so we felt this technique could be useful for this separation.

#### MATERIALS AND METHODS

A total of 112 colorless natural and synthetic sapphires were characterized for this study. The 72 natural samples were all faceted stones. They ranged

Figure 8. Although cathodoluminescence has been used to reveal the characteristic straight growth bands in this natural colorless sapphire, these bands often can be observed with long-wave UV radiation or immersion microscopy. Photomicrograph by Shane Elen; magnified 3.5x.



from 0.05 to 3.08 ct (2.0–8.4 mm) and originated from Sri Lanka (66), Montana (1), Myanmar (1), Umba (1), and unknown sources (3). The synthetic sapphires consisted of 39 faceted samples (0.05–3.82 ct, 2.0–9.5 mm) and one Verneuil-grown half boule (18.3 ct). The faceted synthetic sapphires included five flame-fusion and four Czochralski-grown samples of known growth method. The 30 remaining faceted synthetic samples were of unknown growth method. In addition, a single 8 mm round brilliant hydrothermal colorless sapphire, which had been grown for experimental purposes (Walter Barshai, pers. comm., 1997), was obtained from Tairus.

Of the 112 samples, the origin of 43 natural and 22 synthetic faceted sapphires was confirmed by the presence of characteristic inclusions or growth structures observed using immersion microscopy or luminescence patterns. The remainder, generally the smaller samples, exhibited no readily identifiable features, so we accepted their origins as represented by the reliable sources who supplied them.

We performed EDXRF analysis on 26 natural and 19 synthetic samples of known origin with a Tracor Spectrace 5000 X-ray system, using conditions established for ruby analysis (see Muhlmeister et al., 1998). The purpose was twofold: to determine the usefulness of this technique to separate natural from synthetic colorless sapphires, and to provide more information about how trace-element content affects the SWUV transparency. EDXRF analysis was restricted to samples greater than 4 mm in diameter (approximately 0.3 ct) because of limitations imposed by the X-ray spot size of this equipment. Absorption spectra were obtained on all 112 samples at room temperature with a Hitachi U4001 spectrophotometer. Spectra for a few of the samples were collected from 250 nm to 750 nm; however, since data above 350 nm were not important for this study, the remaining analyses were collected in the UV range from 250 nm to 350 nm.

At the request of GIA, John Schnurer of Physics Engineering (Yellow Springs, Ohio) constructed a SWUV transparency instrument for the separation of natural from synthetic colorless sapphire (see Box A). This instrument was based on the phosphoroscope originally proposed by Yu and Healey (1980), and was constructed to provide a relatively simple, rapid, and cost-effective means of separation.

## RESULTS

**Chemical Composition.** The natural sapphire samples typically contained three or more trace ele-



Figure 9. Curved striae cannot be detected in colorless synthetic sapphires with standard visible lighting. However, some flame-fusion synthetic sapphires may reveal this feature when exposed to SWUV radiation. Photomicrograph by Shane Elen; magnified 6x.

ments (table 1; figure 10). The most significant was iron (Fe); other elements recorded include titanium (Ti), calcium (Ca), and gallium (Ga). Vanadium (V) and chromium (Cr) were only detected at concentrations just exceeding the detection limit of the instrument. In general, no trace elements were detected in the flame-fusion and Czochralski-grown synthetic sapphires, although some samples showed very small amounts of Ca, Ti, and Fe—again, just exceeding the detection limit. The iron content was much greater in the natural sapphires (0.021–0.748 wt.% FeO) than in the synthetic sapphires (up to 0.007 wt.% FeO; table 1). Qualitative analyses of the hydrothermal synthetic sapphire showed significant amounts of Fe, Ga, cobalt (Co), and copper (Cu).

**UV-Visible Spectrophotometry.** Table 1 lists the wavelengths for the absorption cutoff of all the samples analyzed by EDXRF. The natural colorless sapphires typically showed a sharp absorption cutoff (i.e., complete absorption) below 280–300 nm, whereas the synthetic sapphires showed at most only a slight increase in absorption at around 250 nm (see, e.g., figure 11). Note that three of the small (about 2 mm) colorless natural sapphires exhibited a gentle increase in absorption, only slightly greater than that of the synthetic samples. The hydrothermal synthetic sapphire exhibited a sharp absorption cutoff at 280 nm, similar to natural sapphire.

**SWUV Transparency.** All 72 natural colorless sapphires tested with the modified phosphoroscope were opaque to SWUV, and all 40 flame-fusion and Czochralski-grown synthetics were transparent to SWUV. The single hydrothermal synthetic sapphire

## BOX A: THE MODIFIED PHOSPHORSCOPE TO TEST SHORT-WAVE UV TRANSPARENCY

The modified phosphoroscope (after Yu and Healey, 1980; figures A-1 and A-2) we constructed for this study consists of a glass plate that has been coated with a specially selected (proprietary) nontoxic phosphor, an overhead short-wave ultraviolet (SWUV) lamp, and a mirror positioned at a 45° angle below the glass plate. To reduce glare, the glass plate and mirror were placed inside a box, with the UV lamp mounted externally. The phosphor-coated glass plate fluoresces when exposed to SWUV radiation (254 nm wavelength), creating a brightfield background.

For testing, we placed the samples table-down on the glass plate, one or more at a time, and observed their transparency to SWUV in the mirror (figure A-3). Samples that are opaque to SWUV (i.e., natural colorless sapphires) do not allow the radiation to pass through the stone to the phosphor-coated plate, so there is no fluorescence where the stone contacts the plate. Consequently, natural colorless

sapphires appear in the mirror as dark spots on a brightfield background. Conversely, samples that are transparent to SWUV (such as melt-grown synthetic colorless sapphires) allow UV radiation to pass through the stone to the phosphor-coated plate. So the Verneuil- and Czochralski-grown synthetic colorless sapphires typically appear in the

*Figure A-1. The SWUV transparency tester was constructed with simple materials: wood, a mirror, a glass plate, and drafting vellum. A Gem Instruments long-wave/short-wave UV lamp is positioned over an opening at the top of the box.*

*The samples are loaded into the upper part of the unit through a door on the back. The number of stones that can be tested depends on the size of the fluorescent plate, which in turn is governed by the size and intensity of the SWUV source; 100 melee-size stones can easily be accommodated in this particular unit. Photo by Maha DeMaggio.*



appeared opaque to SWUV. Some of the natural and synthetic colorless sapphires acquired a slight brown bodycolor as a result of their exposure to SWUV radiation. However, they returned to their original color after gentle heating under the bulb of an incandescent desk lamp (Kammerling and McClure, 1995).

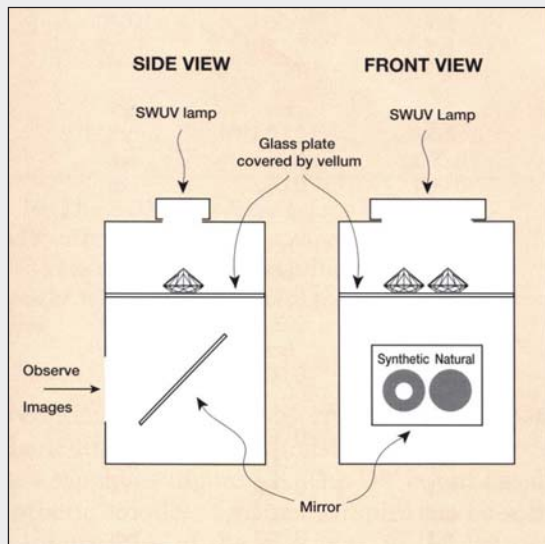
## DISCUSSION

The higher concentrations of Fe, Ti, and Ga aid in distinguishing natural colorless sapphire from the synthetic material. However, Fe is the dominant impurity in natural colorless sapphire, where it is present in quantities typically 10 to 100 times greater than in its synthetic counterpart. The

mirror as light spots, each of which is surrounded by a dark perimeter, imposed on the brightfield background. The dark perimeter results from total internal reflection of the incident radiation as it passes through the pavilion and strikes the bezel facets. Therefore, it is important when testing the transparency to observe only the response in the central part of the gem (Yu and Healey, 1980).

Following the lead provided by Yu and Healey (1980), one of the authors (SE) subsequently modified this unit by replacing the proprietary phosphor with a readily available translucent paper product (drafting vellum) that has all the necessary fluorescence characteristics described above. This product

*Figure A-2. This schematic diagram of the SWUV transparency unit shows how the image of the samples that have been illuminated by the UV lamp is reflected toward the viewer. This also illustrates the appearance, observed in the mirror, of a natural sapphire (right) as compared to its synthetic counterpart (left).*

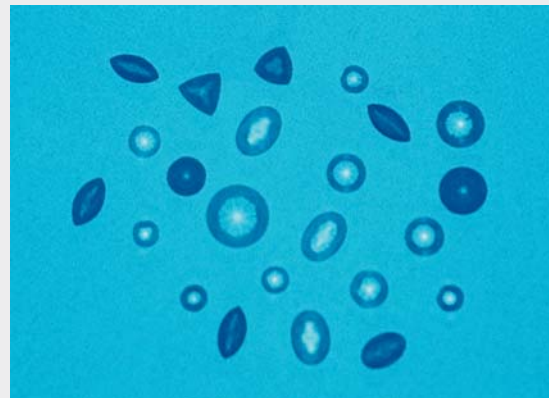


is more uniform than the proprietary phosphor, and it has brighter fluorescence characteristics; it is also inexpensive, clean, and nontoxic.

The modified phosphoroscope is simple to construct from inexpensive materials (about \$30 excluding the UV source). Those interested in constructing a SWUV transparency tester should review the limitations listed in the Discussion and note the following recommendations:

1. Wear UV-protective glasses, and take precautions not to expose unprotected skin to the SWUV radiation when the gems are sorted by hand.
2. Use known samples of natural and synthetic colorless sapphires as standards for evaluating the reactions of the unknown stones. These "control" samples should be 3 to 4 mm in diameter and free from abundant eye-visible inclusions. These may also be useful in selecting the appropriate paper product for the luminescent screen when constructing a phosphoroscope.

*Figure A-3. When viewed with the SWUV transparency tester, the natural colorless sapphires appear opaque, while the synthetic samples are transparent, resulting in a bright spot in their central regions. These samples range from 0.20 to 2.12 ct. Photo by Shane Elen.*



hydrothermal synthetic sapphire also contained Fe and Ga, but it showed distinctive Co and Cu, too—neither of which was detected in any of the other samples. The impurities detected in natural sapphires (i.e., Fe, Ti, Ca, and Ga) are present essentially as transition metal ions, so their absorptions affect the ultraviolet transparency of the colorless sapphires as measured by UV-visible spectropho-

tometry. The absorption is due to charge-transfer processes, as well as to electronic transitions of isolated metal ions (McClure, 1962). Although all the transition impurities induce absorption in the UV, iron is the primary cause because its absorption is situated closer to the visible range and it is the dominant impurity in the natural material. Consequently, we plotted the relationship between



**TABLE 1.** Semi-quantitative EDXRF data and UV absorption maxima for natural and synthetic colorless sapphires.

Sample no.	Weight (ct)	Oxide (wt.%)						UV abs. <sup>a</sup> (nm)
		CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	Ga <sub>2</sub> O <sub>3</sub>	
<b>Natural</b>								
1433	3.08	bdl <sup>b</sup>	0.006	bdl	bdl	0.066	0.033	292
1447 <sup>c</sup>	2.10	0.061	0.030	bdl	bdl	0.090	0.055	300
2190	0.78	0.047	0.036	0.003	bdl	0.116	0.012	292
2191	1.10	bdl	0.032	0.004	0.002	0.246	0.019	298
2336	1.84	bdl	0.018	bdl	bdl	0.117	0.003	293
2348 <sup>c</sup>	0.33	0.045	0.048	0.004	bdl	0.099	0.005	293
2349 <sup>c</sup>	0.19	0.069	0.049	bdl	bdl	0.091	0.008	290
2885	0.84	0.021	0.016	0.005	0.015	0.748	bdl	310
2886	2.75	bdl	0.018	0.002	bdl	0.058	0.013	290
4009	0.98	0.011	0.033	0.005	0.002	0.046	0.018	290
4010	0.94	bdl	0.018	bdl	bdl	0.079	0.005	292
4011	0.59	0.029	0.031	bdl	bdl	0.097	0.014	290
4012	0.64	0.039	0.026	bdl	bdl	0.122	0.011	292
4013	0.76	0.016	0.022	0.003	0.006	0.096	0.014	288
4014	0.75	bdl	0.013	bdl	bdl	0.042	0.005	284
4015	0.49	0.039	0.065	bdl	bdl	0.048	0.016	282
4016	0.42	0.041	0.028	bdl	bdl	0.134	0.015	291
4017	0.60	0.039	0.024	bdl	bdl	0.021	0.014	280
4018	0.33	0.048	0.043	0.004	bdl	0.091	0.011	290
4019	0.33	0.029	0.028	bdl	bdl	0.148	0.013	292
4020	0.47	0.037	0.011	bdl	bdl	0.179	0.013	291
4021	0.42	0.060	0.010	bdl	0.003	0.108	0.012	292
4022	0.32	0.066	0.017	bdl	bdl	0.276	bdl	296
4023	0.61	0.029	0.028	0.005	bdl	0.055	0.023	288
4024	0.74	0.017	0.036	0.006	bdl	0.059	0.020	291
4025	0.57	0.017	0.024	0.004	bdl	0.070	0.017	292
<b>Synthetic – Czochralski</b>								
1635	0.89	0.022	bdl	bdl	bdl	bdl	bdl	<250
2334	0.91	0.017	bdl	bdl	bdl	0.003	bdl	<250
2352	0.98	0.027	0.009	bdl	0.003	0.004	bdl	<250
2353	1.01	0.024	bdl	bdl	0.004	0.002	bdl	<250
<b>Synthetic – Flame Fusion</b>								
2335	2.81	bdl	0.005	bdl	bdl	bdl	bdl	<250
2509	18.30	bdl	bdl	bdl	bdl	bdl	bdl	<250
2887	2.44	0.016	0.009	bdl	bdl	0.002	bdl	<250
2888	2.12	bdl	0.005	bdl	bdl	0.002	bdl	<250
2889	2.49	bdl	bdl	bdl	bdl	bdl	bdl	<250
2890	1.45	bdl	bdl	bdl	0.003	0.002	bdl	<250
<b>Synthetic – Unspecified Method of Synthesis</b>								
3931a	1.12	0.019	0.009	bdl	bdl	0.003	bdl	<250
3931b	1.06	0.028	bdl	bdl	bdl	0.005	bdl	<250
3931c	0.99	0.015	bdl	bdl	bdl	0.002	bdl	<250
3931d	1.06	0.018	0.006	0.003	bdl	0.004	bdl	<250
3932a	0.66	bdl	0.006	bdl	bdl	0.003	bdl	<250
3932b	0.64	0.024	bdl	bdl	bdl	bdl	bdl	<250
3932c	0.61	0.038	bdl	bdl	bdl	0.007	bdl	<250
3933	3.82	bdl	bdl	bdl	bdl	bdl	bdl	<250
3934	1.10	0.014	bdl	bdl	bdl	0.003	bdl	<250
<b>Detection Limits<sup>d</sup></b>								
	0.3	0.019	0.009	0.004	0.004	0.004	0.005	
	0.6	0.013	0.005	0.003	0.003	0.003	0.003	
	1.0	0.009	0.005	0.003	0.002	0.002	0.002	

<sup>a</sup>For the synthetic samples, the absorption cutoff did not occur in the measured region above 250 nm, so we infer <250 nm.

<sup>b</sup>bdl = below detection limit. MnO was looked for, but not detected in any of the samples.

<sup>c</sup>Three samples also contained traces of Si, probably due to the presence of silicate inclusions: 1447 = 0.251 wt.% SiO<sub>2</sub>, 2348 = 0.396 wt.% SiO<sub>2</sub>, and 2349 = 0.428 wt.% SiO<sub>2</sub>.

<sup>d</sup>Detection limits vary according to the weight of the sample. Calculated after Jenkins (1980).

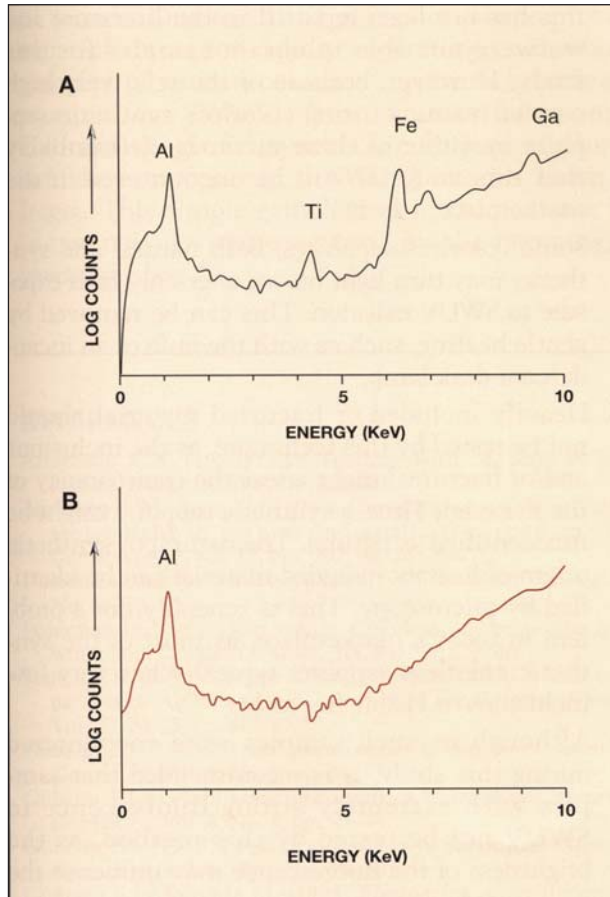


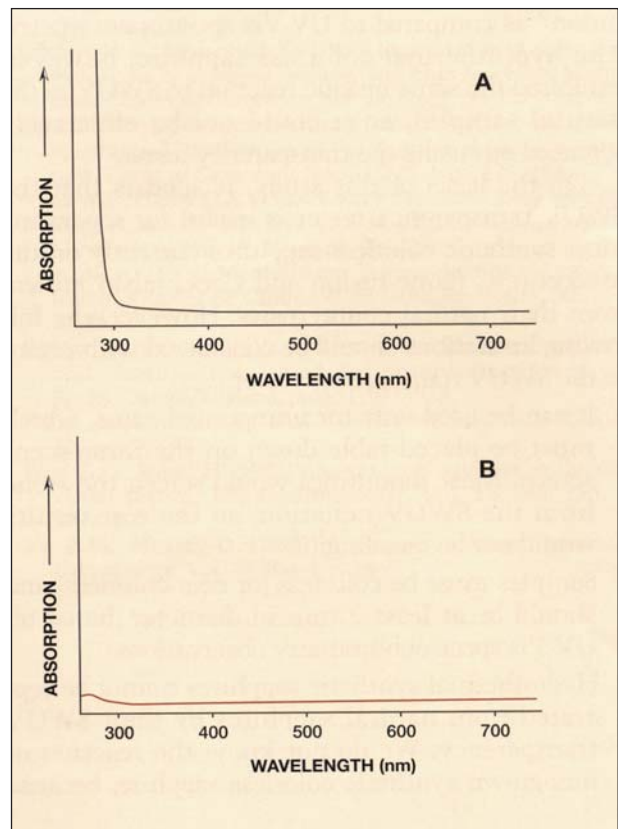
Figure 10. The EDXRF spectra typical of natural (A) and synthetic (B) colorless sapphires are distinct. The natural sapphires exhibit more trace-element peaks (e.g., Fe, Ti, and Ga) than the synthetic sapphires.

the Fe content and the UV absorption cutoff for natural, flame-fusion, and Czochralski-grown synthetic colorless sapphires (figure 12). The UV cutoff for all the synthetic colorless sapphire samples can be seen at the intersection of the two axes, in the bottom left corner of the plot (at 250 nm). In reality, this point only represents a slight increase in absorption, and the true cutoff occurs below 250 nm (i.e., below the wavelength range of the UV-Vis spectrophotometer used for this study). Together, the EDXRF and the UV-Vis data illustrate the effect of trace-metal impurity concentrations on SWUV transparency; in particular, they show how the increase in iron content results in a decrease in SWUV transparency.

For the natural colorless sapphires, the sharp increase (or cutoff) in SWUV absorption below

280–300 nm indicates complete absorption, and therefore the point at which they become opaque to SWUV radiation. With the exception of the hydrothermal sample—which showed an absorption cutoff at 280 nm, and therefore could not be separated from natural sapphire using UV-Vis spectrophotometry—the synthetic colorless sapphires exhibited only a slight increase in SWUV absorption around 250 nm, which indicates that they are relatively transparent to SWUV. Although most of the small (2 mm) natural sapphires exhibited a sharp absorption edge, a few did not. Certainly, some natural colorless sapphires with low impurity concentrations may be thin enough to allow some transmission of SWUV. In our sample, this appeared to be the case particularly for the few melee stones

Figure 11. These UV-Vis spectra are representative of natural (A) and synthetic (B) colorless sapphires. The natural samples show a sharp absorption cutoff below 280–300 nm, whereas no cutoff is evident in this region for the synthetic sapphires. Therefore, the natural sapphires were opaque to SWUV radiation (at 254 nm), but the synthetic samples were transparent.



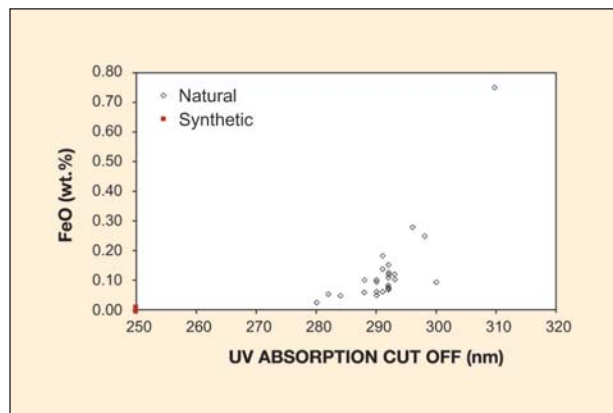


Figure 12. Iron is the primary cause of absorption in colorless sapphire. In general, the natural sapphires analyzed in this study showed higher UV absorption values with increasing iron content. The synthetic sapphires (19 represented here) all showed very low iron contents (<0.007 wt.% FeO), and had UV cutoffs below the wavelength for SWUV radiation (~250 nm).

that were cut with shallow pavilions. Nevertheless, these samples appeared opaque in the SWUV transparency tester, perhaps because of the lower “resolution” as compared to UV-Vis spectrophotometry. The hydrothermal colorless sapphire, however, exhibited the same opaque reaction to SWUV as the natural samples, so it could not be effectively screened out using the transparency tester.

On the basis of this study, it appears that the SWUV transparency tester is useful for separating most synthetic colorless sapphires currently on the market (i.e., flame-fusion and Czochralski grown) from their natural counterparts. However, the following limitations should be considered with regard to the SWUV transparency tester:

1. It can be used only for unmounted gems, which must be placed table down on the fluorescent screen. Most mountings would screen the stone from the SWUV radiation, so the test results would not be meaningful.
2. Samples must be colorless (or near-colorless) and should be at least 2 mm in diameter (based on UV-Vis spectrophotometry observations).
3. Hydrothermal synthetic sapphires cannot be separated from natural sapphires by their SWUV transparency. We do not know the reaction of flux-grown synthetic colorless sapphire, because

this has not been reported in the literature and we were not able to obtain samples for this study. However, because of the relatively high cost of manufacturing colorless synthetic sapphire by either of these methods, it is unlikely that this material will be encountered in the marketplace.

4. Some colorless sapphires, both natural and synthetic, may turn light brown after only brief exposure to SWUV radiation. This can be removed by gentle heating, such as with the bulb of an incandescent desk lamp.
5. Heavily included or fractured material should not be tested by this technique, as the inclusions and/or fractures might affect the transparency of the material. Thus, a synthetic sapphire might be misidentified as natural. The natural or synthetic origin of heavily included material can be identified by microscopy. This is generally not a problem in today’s marketplace, as most of the synthetic colorless sapphire typically has very few inclusions or visible fractures.
6. Although no such samples were encountered during this study, it is recommended that samples with extremely strong fluorescence to SWUV not be tested by this method, as the brightness of the fluorescence may influence the “apparent” opacity of the sample and result in an incorrect identification.

## CONCLUSION

With standard gemological techniques, only one colorless sapphire at a time can be investigated. In addition, it is usually more difficult to identify smaller stones, because they commonly do not show any diagnostic features. The advanced techniques of EDXRF analysis and UV-Vis spectrophotometry are also useful to separate most natural and synthetic colorless sapphires. Our trace-element data illustrate that, in general, natural colorless sapphires contain greater amounts of Fe, Ti, Ca, and Ga than do their synthetic counterparts. UV-Vis data further confirm that synthetic colorless sapphires are more transparent to SWUV, because they exhibit only a small increase in absorption at approximately 250 nm. By comparison, natural colorless sapphires typically exhibit total absorption below 280–300 nm.

However, EDXRF and UV-Vis spectrophotometry are not readily available to most gemologists; nor are they economical for testing large quantities

of stones. Our modified phosphoroscope proved most effective for rapidly separating unmounted samples of natural colorless sapphires (which are opaque to SWUV) from flame-fusion and Czochralski-grown synthetic colorless sapphires (which are transparent to SWUV), in sizes 2 mm or larger. This simple gemological instrument can be inexpensively manufactured by the gemologist (again, see box A).

The SWUV transparency tester cannot be used to separate natural sapphire from hydrothermal synthetic sapphire. However, the relatively high cost of producing colorless hydrothermal synthetic sapphire (Walter Barshai, pers. comm., 1997) precludes its widespread use by the jewelry industry. If necessary, in most cases results from the SWUV transparency test can be confirmed with a gemological microscope.

## REFERENCES

- Anderson B.W. (1990) *Gem Testing*, 10th ed. Rev. by E.A. Jobbins, Butterworth & Co., London.
- Anderson B.W., Payne C.J. (1948) Absorption of visible and ultraviolet light in natural and artificial corundum. *The Gemmologist*, Vol. 17, No. 207, pp. 243–247.
- Demand strong for white sapphires (1996) *Jewellery News Asia*, No. 147, p. 84.
- Federman D. (1994) Gem profile: Colorless sapphire—The great white hope. *Modern Jeweler*, Vol. 93, No. 8, p. 44.
- French R.H. (1990) Electronic band structure of Al<sub>2</sub>O<sub>3</sub> with comparison to AlON and AlN. *Journal of the Ceramic Society*, Vol. 73, No. 3, pp. 477–489.
- Gübelin E.J. (1942a) Local peculiarities of sapphires. *Gems & Gemology*, Vol. 4, No. 3, pp. 34–39.
- Gübelin E.J. (1942b) Local peculiarities of sapphires. *Gems & Gemology*, Vol. 4, No. 4, pp. 50–54.
- Gübelin E.J. (1943) Local peculiarities of sapphires. *Gems & Gemology*, Vol. 4, No. 5, pp. 66–69.
- Gübelin E.J., Koivula J.I. (1992) *Photoatlas of Inclusions in Gemstones*. ABC Edition, Zurich, Switzerland.
- Jenkins R. (1980) *An Introduction to X-ray Spectrometry*. Heyden, Philadelphia.
- Kammerling R.C., DeGhionno D., Madison P. (1994) Gem Trade Lab notes: Synthetic sapphire, another striae resolution technique. *Gems & Gemology*, Vol. 30, No. 4, p. 270.
- Kammerling R.C., Koivula J.I. (1995) Microscope lighting techniques for identifying melt-grown synthetics. *Bangkok Gems and Jewellery*, Vol. 8, No. 7, pp. 88–94.
- Kammerling R.C., McClure S.F. (1995) Gem Trade Lab notes: Synthetic sapphire, with color changed by UV radiation. *Gems & Gemology*, Vol. 31, No. 4, p. 271.
- Kane R.E., Kammerling R.C., Koivula J.I., Shigley J.E., Fritsch E. (1990) The identification of blue diffusion-treated sapphires. *Gems & Gemology*, Vol. 26, No. 2, pp. 115–133.
- Kane R.E. (1990) Gem Trade Lab notes: Sapphire—Large colorless. *Gems & Gemology*, Vol. 26, No. 3, pp. 225–226.
- Keller P.C. (1982) The Chanthaburi-Trat gem field, Thailand. *Gems & Gemology*, Vol. 18, No. 4, pp. 186–196.
- Koivula J.I., Kammerling R.C., Fritsch E. (1992) Gem news: Update on diffusion-treated sapphires. *Gems & Gemology*, Vol. 28, No. 1, pp. 62–63.
- Liddicoat R.T. Jr. (1987) *Handbook of Gem Identification*, 12th ed. Gemological Institute of America, Santa Monica, CA.
- McClure D.S. (1962) Optical spectra of transition-metal ions in corundum. *Journal of Chemical Physics*, Vol. 36, No. 10, pp. 2757–2779.
- Muhlmeister S., Fritsch E., Shigley J.E., Devouard B., Laurs B.M. (1998) Separating natural and synthetic rubies on the basis of trace element chemistry. *Gems & Gemology*, Vol. 34, No. 2, pp. 80–101.
- Nassau K. (1980) *Gems Made By Man*. Chilton Book Co., Radnor, PA.
- Plato W. (1952) Oriented lines in synthetic corundum. *Gems & Gemology*, Vol. 7, No. 7, pp. 223–224.
- Ponahlo J. (1995) Cathodoluminescence (CL) of gemstones and ornamental stones. *Analisis*, Vol. 23, No. 1, pp. M30–M33.
- Rubin J.J., Van Uitert L.G. (1966) Growth of sapphire and ruby by the Czochralski technique. *Materials Research Bulletin*, Vol. 1, pp. 211–214.
- Schmetzer K., Medenbach O. (1988) Examination of three-phase inclusions in colorless, yellow, and blue sapphires from Sri Lanka. *Gems & Gemology*, Vol. 24, No. 2, pp. 107–111.
- Smith C.P. (1996) Introduction to analyzing internal growth structures: Identification of the negative *d* plane in natural ruby. *Gems & Gemology*, Vol. 32, No. 3, pp. 170–184.
- Stern W.B., Hänni H.A. (1982) Energy dispersive X-ray spectrometry: A non-destructive tool in gemmology. *Journal of Gemmology*, Vol. 18, No. 4, pp. 285–296.
- Verneuil A. (1904) Memoire sur la reproduction du rubis par fusion. *Annales de Chimie et de Physique*, Ser. 8, No. 3, pp. 20–48.
- Webster R., Read P.G. (1994) *Gems: Their Sources, Descriptions and Identification*, 5th ed. Butterworth-Heinemann Gem Books, Oxford, England, pp. 851, 931–933.
- White sapphire sales up 172% (1994) *Jewellery News Asia*, No. 120, pp. 92–94.
- Wild G.O., Biegel H. (1947) Absorption of sapphire in the ultraviolet region. *The Gemmologist*, Vol. 16, No. 195, pp. 279–280.
- Yu R.M., Healey D. (1980) A phosphoroscope. *Journal of Gemmology*, Vol. 17, No. 4, p. 250.