An Introduction to Spectroscopy

in

Gemtesting

by

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Adapted from a lecture delivered to the American Gem Society Conclave, Philadelphia, April, 1957.

It has been nearly a hundred years since Sir Arthur Church first described absorption bands in gemstones as seen through a spectroscope, but the credit for establishing the instrument soundly in the list of "musts" for the gemologist must go to men now living. Actually, it has been only in the past thirty years or so that gemologists, headed by B. W. Anderson, Director of Precious Stone Laboratory of the London Chamber of Commerce, have described and recorded the results to be expected from this instrument.

A spectroscope is essentially an instrument that will spread light into its component wavelengths. It is well known to most of us that white light is composed of the colors of the spectrum and that each color has a characteristic wavelength. Visible light is actually only part of a series that varies in wavelength from the relatively gigantic wavelengths of electricity and radio; through

infrared; to the visible wavelengths that diminish in wavelength from red; through orange, yellow, green, blue, and violet; passing into the even shorter and invisible ultraviolet, X ray and gamma rays; and finally to cosmic rays. The whole is known as the electro-magnetic spectrum. In order to measure visible light, a unit of measurement, the Angstrom unit, is used; it is 1/10,000,000 of a millimeter. For practical purposes, we usually think of the visible spectrum as extending from a bit more than 7000 Å to 4000 Å.

One of the first men to study sunlight through a prism was Sir Isaac Newton. Many of us, I am sure, are familiar with the picture of him holding a prism in the path of sunlight streaming through a small opening in a shutter of an otherwise darkened room. Perhaps the first man to advance spectroscopy in a manner leading to its use with gem minerals was Joseph Fraunhofer (1787-

1826). He studied the spectrum produced by sunlight. He noted that his prism not only separated light into the component colors of the spectrum, which we see in a rainbow, but he also noted many dark lines, the strongest of which today are known as "Fraunhofer's lines." Angstrom, the great Swedish physicist, mapped the solar spectrum in 1869 with a spectrum containing more than 1000 lines. One of the most persistent lines in the spectrum of the sun is actually a pair of emission lines at 5896 and 5890 Å. It was about a hundred years ago that the significance of these lines was discovered; they are due to sodium. Since that time, the causes of most of the other lines in the sun's spectrum have been found to be due to vaporized elements in the sun's atmosphere (as well as our own). With these initial discoveries, the spectroscope was turned to other uses, among which can be mentioned its part in the discovery of both ultraviolet and infrared wavelengths - both invisible to the human eye. The spectroscope's use in the study of astronomy is well known, as is the fact that it was used in discovering helium, an element apparently missing in the sun's spectrum. In 1833, David Brewster described the typical broad absorption bands in blue glass as being due to cobalt. His was the first use of the instrument on a cold solid. Today, commercial spectroscopes find great use in the analysis of chemical elements, blood samples, etc. Through the vaporization of various compounds, as little as 2% of certain elements in a compound can be detected. For this purpose, elaborate instruments, many too expensive or unwieldly for the gemologist, are made.

The spectroscopes recommended for use with gem materials are of two types, both of which are available in small size and are known as hand spectroscopes. Perhaps the most serviceable is the direct-vision prism spectroscope, in which the spectrum is produced by the use of three glass prisms, two of crown glass and one of flint glass. An-

other type uses a diffraction grating on glass instead of prisms to separate the light into its colors. It has the advantage of producing a spectrum that is more evenly spread, whereas the prism type concentrates the red end of the spectrum but extends the blue end. However, the diffraction-grating spectroscope requires much more light, with the result that the prism type is usually regarded as the more satisfactory for other than strict laboratory setups. All spectroscopes for use in gem testing should have an adjustable slit to control the amount of light that enters the instrument. In addition, some spectroscopes are made in which two spectra can be observed for comparison purposes, and others in which a scale marked in Angstrom units from 7000 to 4000 is superimposed, thus permitting actual measurement of the absorption lines observed.

Although the first use of the spectroscope was to observe lines brought about through the vaporization of substances resulting in emmission spectra, the use of the spectroscope with gems requires an understanding of absorption spectra.

The color of a transparent gemstone is the result of selective absorption and transmission of light that passes through the material. Therefore, if a beam of light is first passed through a stone and then onto the prism of a spectroscope, it is dispersed into the familiar spectrum, and it is sometimes possible to see the results of this selective absorption imposed on the light by the stone as dark bands crossing the spectrum vertically. For example, if a stone fails to pass any yellow light, the spectrum will be complete in all colors except yellow. In other words, the stone absorbs the yellow and the spectroscope shows this by a dark band varying in width according to the wavelengths absorbed by the stone. Absorption bands for gemstone may be exceedingly sharp and narrow or wide enough to cover large parts of the spectrum. In addition, the width and appearance of the absorption bands may vary from specimen to specimen

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of the same species and variety.

Only a small number of common gemstones absorb a sufficient amount of light in various portions of the spectrum to result in absorption bands or lines that are visible with the hand spectroscope. At times, a normally reliable variety may fail to show the bands expected, or not as prominently as expected.

For some gemstones the cause of the absorption bands may be ascribed to the definite presence of certain elements. In other cases the cause may be unknown or uncertain.

One element that is known definitely to be responsible for absorption bands in several stones is chromium. Chromium is known to be responsible, moreover, for the colors that we see in most of these stones. For convenience, the absorption of chromium-colored gemstones can be divided into two groups: red and green.

The red group includes ruby (and, unfortunately, for distinguishing between them, synthetic ruby), natural red spinel, chrome pyrope (typically from Arizona), and pink topaz. Chromium absorption bands are found mainly in the red end of the spectrum.

Another metallic element known to be the cause not only of the color but of the characteristic spectrum of gem materials is iron. The grouping here depends on the valence of the iron and can be separated into the ferric group and the ferrous group. In the former are natural green and blue sapphires, demantoid garnet, yellow and brown chrysoberyl, and epidote. In the ferrous group are included almandite garnet, peridot, and blue spinel. Absorption bands caused by iron are mainly found toward the blue end of the spectrum.

Zircon may have as many as 16 bands or, for some natural reddish-brown colors, none at all. The strongest band, at 6535 Å, may frequently be the only one present and is usually visible even in heated blue and colorless stones. The spectrum is believed to be caused by uranium.

A final group of absorption spectra is caused by unknown or uncertain elements, the most important of which is diamond. A narrow band in the deep blue at 4155 Å is most commonly observed, particularly in slightly yellowish and Cape-colored diamonds and especially pronounced in those that fluoresce blue in ultraviolet light. Some rare stones that have a brown to greenish-yellow body color and that fluoresce a greenish color show a strong band at 5040 Å, along with other bands.

The observation of colored diamonds in the spectroscope has been somewhat confused by the appearance in the jewelry trade of brown and golden-yellow cyclotron- and atomic-pile-treated stones, in which the artificially induced color often prevents the observation of the original ultraviolet fluorescence.

Recently, in observing a large yellow diamond in the New York Laboratory, we noted a strong line in the spectrum at approximately 5960 Å, which appears just a bit beyond the sodium line used as a scale regulator. We were unable to discover any reference in gemological literature to the occurrence of this line in diamond. On a hunch, we requested permission of Mr. Theodore Moed, a dealer in cyclotroncolored diamonds, to examine as many treated yellow stones as possible. To our surprise, we noted this line in every treated yellow stone, whether pile or cyclotron treated. Correspondence with Mr. B. W. Anderson, in London, brought the information that he has observed a weak line in natural yellow diamonds but so rarely that it was not included in his recent comprehensive serialized discussion of the spectroscope, in The Gemmologist. We thereupon sought as many purportedly untreated yellow diamonds as possible to examine. Of some 62 stones, the only one in which we detected this weak line was a small greenish-yellow .61-carat stone that fluoresced an intense green. Although we cannot at present base a definite identification of artificial coloration upon the presence of this line in the absorption spectrum of yellow diamonds, we hope that further work may produce positive evidence of its value.

Cobalt, which is used for coloring both synthetic blue spinel and some blue glasses, gives a characteristic absorption spectrum consisting of three broad bands in the red, yellow and green. Vanadium, which is used to color synthetic alexandrite sapphire, gives, in addition to a general absorption of the orange and yellow and violet, a narrow line at 4750 Å, which can be useful in identification.

At Eastern Headquarters we are frequently asked when we find the spectroscope most useful. In thinking about this question, I recall a visit we had from a student. He arrived late in the day and we were under considerable pressure for time, but I did want to see his collection of more than 60 colored stones and to check his identifications for him. With only the spectroscope and an observation of the color, it may surprise the reader to know that I was able to identify more than half of the stones. In a few of the fancy sapphires it was necessary to check for natural origin, either by eye or with the microscope. It was possible to identify quickly each of the more than a dozen fancy zircons, the peridots, natural blue sapphires, alexandrites, blue and red spinels, green garnets, yellow chrysoberyls, and even one sinhalite! The spectroscope was of no help, of course, with the fancycolored spinels, topazes, yellow Ceylon sapphires, tourmalines, or quartz stones. Nevertheless, the entire parcel of stones required less than 15 minutes to identify, including the use of the polariscope, the refractometer, and the microscope, with those stones where the spectroscope was of little or no help.

Recently, we found a situation in which the spectroscope was of great value: the identification of the newly marketed dyed jadeite. Here, instead of the three bands in the red that are seen in similarly colored natural material, we noted one broad band in the medium red. The characteristic jadeite band at 4370 Å was missing, because it was masked by the absorption band caused by the dye. The line appears, however, when the color is removed with acid, alum, or heat. The "Imperial-green" jadeite doublets (triplets?) show an even stronger band in the red than the dyed material. We have also noted this same absorption band in green-dyed serpentine.

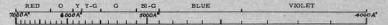
Frequently, ultraviolet light is needed in addition to the spectroscope to identify a flawless natural-yellow sapphire. It has been fairly well established that the two main sources of yellow sapphires are Ceylon and Australia. We find that Ceylon stones fluoresce pinkish yellow, unless their color has been temporarily deepened with Xrays. Australian stones have characteristic absorption bands in the blue. Synthetics show neither.

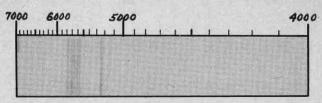
In the Laboratory we often find the spectroscope useful in separating small almandites from dark rubies, especially if they are in closed mountings. It is also very helpful with natural blue sapphires, since the line in the blue is almost always seen in the natural but not in the synthetic. Ruby cannot be separated from synthetic ruby, nor can the Chatham synthetic emerald be separated from its natural counterpart with the spectroscope.

Some of the less frequently encountered gemstones have distinct absorption spectra. The spectrum of yellow apatite, for example, is thought to be caused by the rare earth praseodymium. Chrome diopside, kyanite, californite, enstatite, epidote, greenishyellow spodumene, spessartite, and iolite have more or less consistent and characteristic absorption spectra that may be very useful, especially, as so often happens, if they are uncut crystals or fragments.

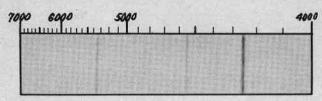
Another frequent question asked is how best to observe the stone and how to set up the light for use with the spectroscope. Various methods have been suggested; e.g.,

TYPICAL ABSORPTION SPECTRA

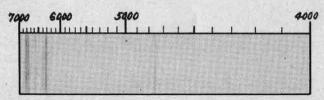




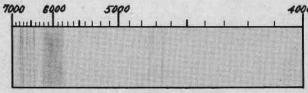
APATITE (green to yellowish green)



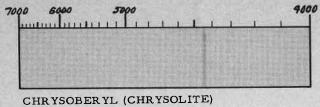
BERYL (AQUAMARINE)

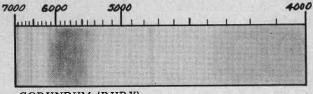


BERYL (EMERALD)

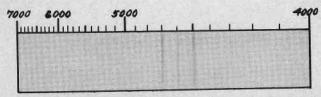


CHRYSOBERYL (ALEXANDRITE)

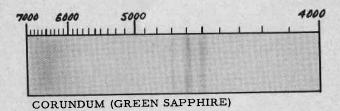


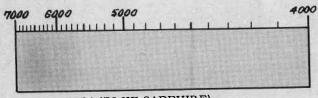


CORUNDUM (RUBY)

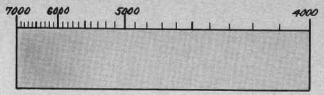


CORUNDUM (yellow Australian sapphire)

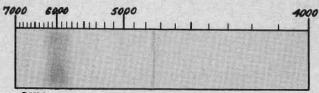




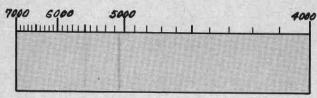
CORUNDUM (BLUE SAPPHIRE)



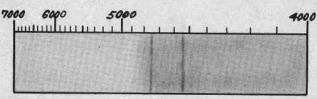
SYN. CORUNDUM (SYN. BLUE SAPPHIRE)



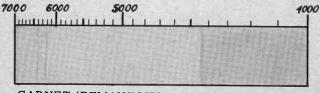
SYN. CORUNDUM (ALEXANDRITE TYPE)



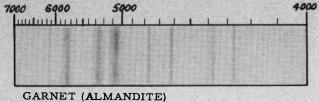
ENSTATITE

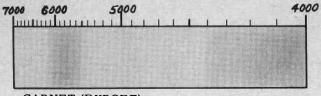


EPIDOTE

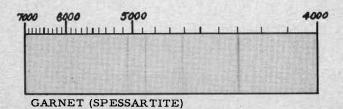


GARNET (DEMANTOID)



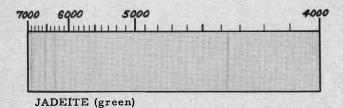


GARNET (PYROPE)

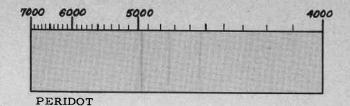


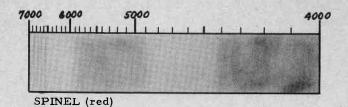
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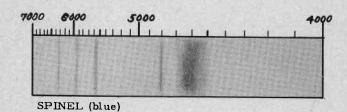
IOLITE

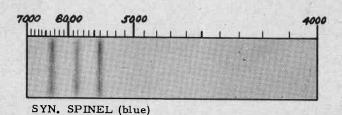


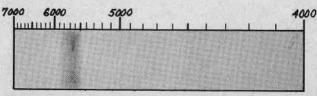
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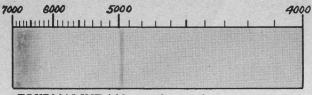




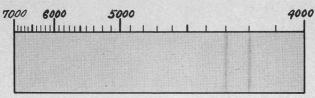




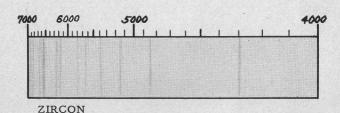
SYN. SPINEL (Alexandrite type)



TOURMALINE (blue and green)



TURQUOIS



using the instrument in place of the eyepiece of a microscope and reflecting a strong light through the stone, placing the stone over a strong light source as one would candle pearls, etc. In the Laboratory, we use a 50-watt bulb in a pearl candler that has openings to accommodate stones of various sizes. If a dark stone is encountered, we sometimes use our 300-watt projector with an adjustable iris diaphragm to allow the light to be focused directly through the stone. Difficulty is sometimes encountered in getting the light through a highly refractive stone. Immersion in a high-index liquid or even smearing the stone with oil will usually allow light to leak through for study. When testing a pale stone, we sometimes place it table down on black velvet and project a strong beam of light through

the pavilion. In this manner the light is reflected from the back side of the table and refracted out the opposite side of the pavilion to the instrument, thus permitting lines to be seen that would not otherwise be visible when using the pearl candler. Some workers have found that a diffused light giving better results can be produced by using a finely ground glass plate directly over the stone in the pearl candler.

The latest models of the Diamondscope and Gemolite, both of which have an iris diaphragm and a 50-watt light source, make a quite convenient arrangement for using the spectroscope with either mounted or, particularly, with unmounted stones.

The most often repeated mistake observed when the novice first begins to use the in(continued on page 62)

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dyed jadeite were being conducted we were shown a cabochon triplet that had been made by hollowing out a piece of nearly colorless, translucent jadeite, filling the depression with an unknown transparent green material, and then cementing to the back of the cabochon a flat piece of jadeite. Mounted in a bezel setting to hide the separation plane, these stones have been reported to sell for hundreds of dollars, as well they might, since they imitate the rare Imperial-green jadeite. Again, the spectroscope gives an immediate indication that something is amiss, since the absorption is "wrong" for natural chrome-colored jadeite. Under magnification, some of the more recent triplets have shown bubbles just under the "shell" of jade at the apex of the cabochon next to the green filling. Out of the mounting, the separation plane of a stone of this type would be visible, thus making identification an easy matter.

DIAMOND SUBSTITUTES

(continued from page 58)

together by any one of various cements, one of the best of which is said to be garlic juice. Careful observation, even with low magnification, will easily identify these doublets, although stones that are mounted with closed bezels can easily be overlooked with just normal inspection under a bright light.

A number of doublets have been made with diamond crowns and other materials used for the pavilion. These include synthetic corundum, quartz, glass, etc. It would not be unreasonable to expect the appearance on the market of doublets consisting of a diamond crown and a strontium titanate pavilion.

GLASS. Glass has probably accounted for the greatest number of diamond substitutes sold in America, if we take into consideration costume jewelry. Rarely, a rather large, beautifully cut piece of glass will be encountered in an expensive mounting as a diamond substitute; however, this combination is unusual. Even the finest glass substitutes do not possess properties that take them out of the range of normal glass, and thus a combination of refractive index and optic character will easily identify them.

AN INTRODUCTION TO SPECTROSCOPY

(continued from page 55)

strument is in not adjusting the slit, which should be manipulated with the left hand in the Beck-Hand instrument. The slit must be adjusted for each stone if the intensity of color varies from the last stone observed; however, it must be as nearly closed as possible and still allow the colors to come through. Frequently, horizontal lines will be seen running the length of the spectrum. These lines are caused by dust in the slit, and it must be carefully removed with a fine brush. A few such lines are not serious; in fact, they usually indicate that the slit is not opened too far.

Depending on the diffusion of the light used, a phenomenon consisting of bright red lines caused by ultraviolet fluorescence may be observed in the far red in rubies, synthetic rubies, and in some red spinels and synthetic red spinels.

Although the spectroscope has been generally slighted in American gemological literature, it is heartening to see that more and more gemologists are working with it and finding it to be a useful instrument.

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