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Enhanced Discrimination of Glass Samples by Phosphorescence Analysis

Of the various types of physical evidence available to crime scene investigators, glass fragments are among those frequently encountered [*1, 2*]. Forensic science examinations usually involve comparing known window glass samples with glass fragments recovered from the suspect's clothing [*3*]. Most crime laboratories use refractive index or density measurements, or both, to compare glass samples. As a result of modern glass production techniques, however, glass formulations are more closely controlled from batch to batch. This results in greater uniformity and reduces the value of analytical techniques that rely on differences in refractive index and density [*4*]. It is generally agreed, therefore, that supplementary analyses are needed.

Trace element analysis procedures that show promise for glass sample discrimination include spark source mass spectrometry [*5,6*], neutron activation analysis [*7*], and X-ray fluorescence analysis [*8*]. The first two procedures can be most discriminating but destroy the sample. (Neutron activation analysis is nondestructive if it is limited to only a few of the trace elements.) Perhaps the most serious drawback of these techniques is the excessive instrumentation cost, which results in limited application. Atomic absorption spectroscopy can be used to reduce the cost, but, again, at least 1 mg of the sample is sacrificed [*3*].

Ideally, the comparison method should be nondestructive, have a high discrimination capability, be capable of analyzing milligram samples, and have an instrumentation cost within the budget of the average crime laboratory. These criteria are met by phosphorescence analysis. Analysis of the low-temperature phosphorescent properties of glass permits differentiation among glass samples that are indistinguishable by their refractive indexes. The procedure used is simple, sensitive, and nondestructive, and the instrumentation cost ($4000 to $10 000) is within the budget restrictions of many crime laboratories.

Phosphorescence is defined here as the light that is emitted from the sample after it has been excited with ultraviolet radiation. The phosphorescence differs from the more familiar fluorescence in that it occurs at longer wavelengths and has a longer lifetime. Thus, if the excitation is turned off, the fluorescence typically decays in nanoseconds or less, whereas the phosphorescence of glass at 77 K takes hundreds of microseconds or longer to decay. This phosphorescence should not be confused with the fluorescence observed from one side of float glass. Special procedures (described in the Experimental Procedures section) are usually required for the detection of phosphorescence from glass samples that also fluoresce.

Anyone who has tried to measure the photoluminescence properties of samples with low luminescence quantum yields is familiar with the difficulty of trying to avoid the luminescence of the glass or quartz container. Only quartz of very high purity can be termed

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"nonfluorescent." It was thought, therefore, that the photoluminescence of glass might be useful for discriminating among samples that could not be distinguished by their bulk properties. The luminescence is emitted by trace impurities in the glass, and it is reasonable to assume that these impurities are not intentionally controlled in the manufacturing process. Of course, it would be expeditious to measure the impurity concentration directly, but there would be disadvantages (such as loss of sample and expense of equipment). Luminescence analysis avoids these disadvantages but is also limited because not all impurities will luminesce. On the other hand, luminescence analysis can often distinguish between elements in different oxidation states and even in different microenvironments. With a judicious selection from the many experimental variables (excitation and luminescence spectra, luminescence yield and lifetime, and temperature effects on all of these), it should be possible to use photoluminescence techniques to distinguish glass samples.

In this paper, the experimental technique is described in some detail. Also presented are the results of an evaluation of phosphorescence analysis as a method for distinguishing among window glass samples that are indistinguishable by their refractive index. In a subsequent paper, the results of the phosphorescence analysis will be compared with the trace element content of the sample; the potential of phosphorescence analysis for distinguishing window and container glass will also be explored.

Experimental Procedures

The 143 glass samples used in this study were originally collected as exemplars for actual cases by the Orange County (California) Sheriff's Office Crime Laboratory. The refractive indexes of the samples were measured with the Abbe refractometer (± 0.0002 precision). The refractive indexes of 21 samples selected for further study were remeasured by the Becke-line method; a monochromator and a Mettler hot stage were used as well as an American Optical Microstar 10 microscope (± 0.0002 precicion). A National Bureau of Standards (NBS) standard reference glass sample was run as an unknown to test the Becke-line procedure. Our measured value for the reference sample was 1.4874; the NBS value is 1.48755. The accuracy of our window glass measurements is not known, however, because measurement of the window glass samples required use of a Cargille Laboratories oil different from that used to measure the NBS sample.

An in-house-fabricated cold-finger Dewar flask (Fig. 1) was used to maintain the glass samples near liquid nitrogen temperature (77 K) during the luminescence analysis. (Similar Dewar flasks are available commercially or can be custom-made by glass blowers.) The optical portion of the Dewar flask was made of quartz to allow transmission of excitation wavelengths as short as 200 nm. The samples may also be cooled by immersion in liquid nitrogen in an optical Dewar flask; however, bubbling of the boiling nitrogen may cause fluctuations in the phosphorescence signal.

Each glass sample was attached to the cold finger with indium according to the following two-step procedure: (1) the finger of the Dewar flask was heated with a clean-tipped soldering gun until approximately 0.1 g of indium was observed to melt, and (2) a chip of glass (previously cleaned with nitric acid) was placed on the molten indium and held firmly in place with a pair of tweezers until the indium solidified. For the larger glass chips, the molten indium was drawn up the edges with the soldering gun. Glass samples attached in this manner are effectively cooled by conduction from the liquid nitrogen reservoir, down the cold finger, through the indium, and into the glass. The Dewar flask was evacuated to 0.1 Pa (10^{-4} torr) before the addition of liquid nitrogen to prevent convectional heating from the outer quartz walls.

A modified Aminco-Bowman Model 4-8202 spectrophotofluorometer was used to record all of the glass luminescence data. No correction was made for instrument response. Modifications to the instrument included a 1200-line/mm grating in the excitation mono-

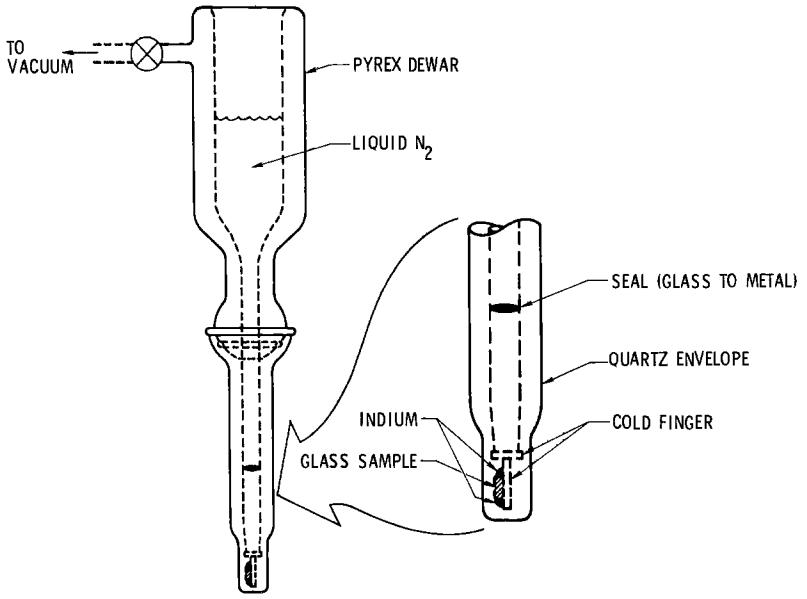

FIG. 1—*Cold finger Dewar flask.*

chromator and a red-sensitive (RCA 31034) photomultiplier. The photomultiplier was maintained at −20 °C in a thermoelectrically cooled housing (Schoeffel Instrument Co., Model D500T). The photomultiplier output was monitored with a Keithley electrometer (Model 417) and a Varian F80 *x-y* recorder. An Aminco-Bowman phosphoroscope (Model 4-8237) was used at a speed of 12 000 rpm. The phosphoroscope is a rotating can that sequentially allows the exciting light to reach the sample, then blocks the excitation, and then, after a short delay (~0.1 ms), allows the luminescence to be detected. In this manner the scattered exciting light and the fluorescence are not detected. Only the phosphorescence with a lifetime comparable to or longer than the delay time is detected.

Only two of the above modifications are required: a phosphoroscope, which prevents detection of scattered exciting light, and a red-sensitive photomultiplier, which is used to detect the longer-wavelength phosphorescence.

Results and Discussion

Refractive Index Measurements

The refractive index distribution of the 143 glass samples is shown in Fig. 2. The glass samples used in the low-temperature luminescence study were from the largest indistinguishable group (21 samples with a mean refractive index of 1.5166 ± 0.0002). When the refractive indexes of these 21 samples were subsequently measured by the Becke-line method, the samples were again indistinguishable.

These results indicate that there is a 0.068 probability that two pieces of glass randomly selected from a set of 143 samples will have the same refractive index (±0.0002). Similar data have been published by others [*9,10*]. It has also been reported that a significant fraction of men's clothing contains glass chips [*11*]. These results attest to the need for analyses that are more discriminating. Various authors have shown that measuring the density rarely provides additional discrimination because of this property's strong correlation with the refractive index [*9,11*].

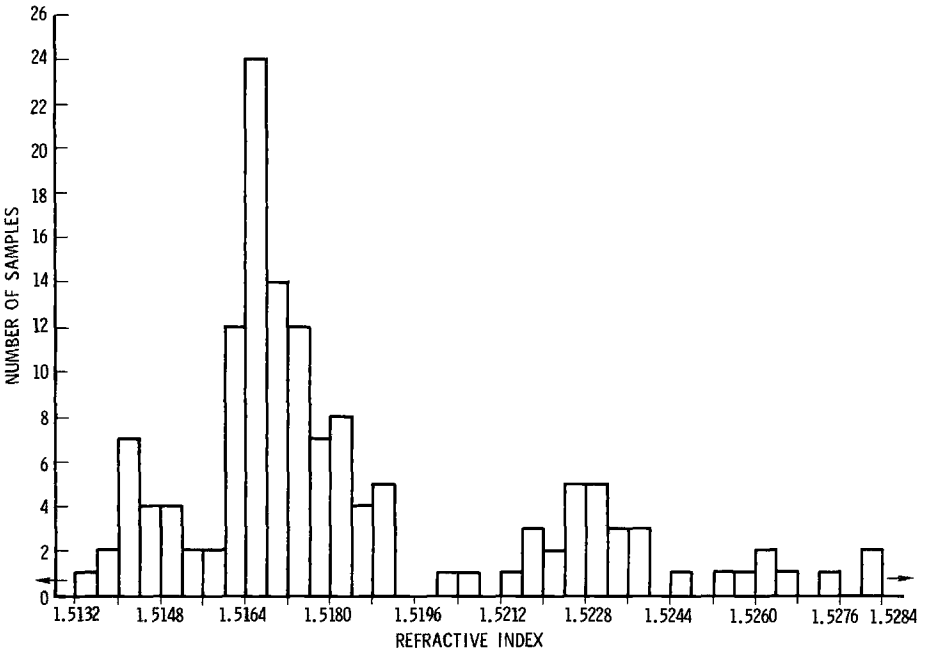

FIG. 2—*Refractive index of 143 glass samples.*

Phosphorescent Properties

The photoluminescence (fluorescence and phosphorescence) of window glass is not intense and can be difficult to detect in the presence of scattered exciting light. By use of a phosphoroscope (described in the Experimental Procedures section), it is possible to exclude the scattered excitation, but this also excludes the fluorescence. Although the fluorescence spectra may provide additional information, a phosphoroscope was found necessary because of the significant scattering that occurs with small, irregularly surfaced glass chips—the type of sample generally available to the criminalist.

Representative phosphorescence spectra of the window glass samples are shown in Fig. 3. With 425-nm excitation of the samples (Fig. 3*a*), the emission spectrum shows two bands, with maxima at 540 and 725 nm. When 325-nm excitation was used (Fig. 3*b*), two bands are again observed, but with maxima at 580 and 740 nm and an apparent shoulder at 700 nm.[2]

As seen in Fig. 3, there are some differences in the shapes of the two bands for different samples, but the main difference is in the relative intensities of the bands. These spectra are for samples cooled by liquid nitrogen, but the spectra for samples at room temperature are identical. The samples were cooled for these exploratory studies because, with cooling, the intensity increases by a factor of approximately 20.

The phosphorescence excitation spectra were also recorded to determine which excitation wavelengths would be most useful for glass sample discrimination and to identify the species responsible for the phosphorescence. (The latter effort has thus far been unsuccessful.) The excitation spectra in Fig. 4 were recorded by monitoring the phosphorescence intensity at 740 nm (I_{740}) and at 550 nm (I_{550}) while varying the excitation wavelength.

[2] Although these spectra have not been corrected for the spectral response of the instrument, the maxima should be close to the correct values because the photomultiplier has a relatively constant response for wavelengths between 300 and 800 nm.

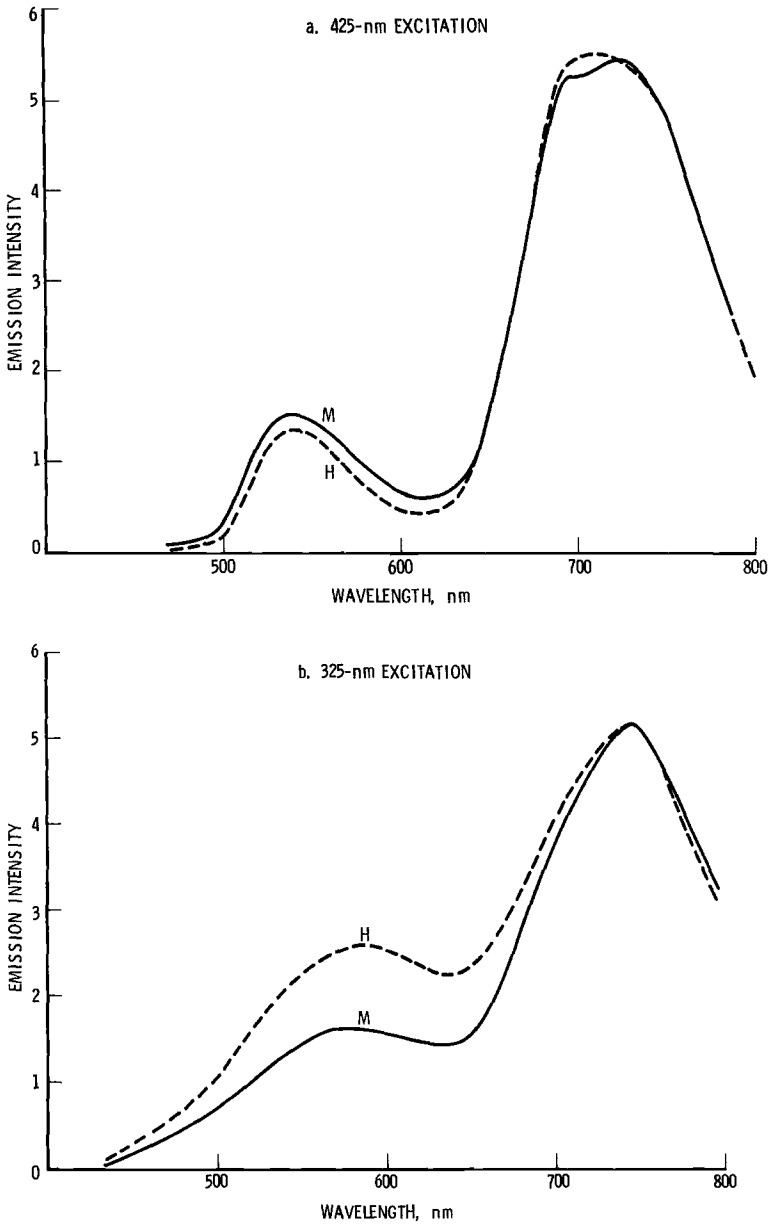

FIG. 3—*Window glass phosphorescence spectra for two windows (designated M and H) and two excitation wavelengths (425 and 325 nm).*

It is seen in Figs. 3 and 4 that the ratio I_{740}/I_{550} strongly depends on the excitation wavelength for wavelengths less than 410 nm.

The excitation spectra, unlike the emission spectra, depend on the thickness of the sample. Figure 5 shows the absorption spectrum of a 2.2-mm-thick glass sample. This sample is not optically thick[3] for wavelengths greater than 320 nm. As a result, the bands

[3] A sample is considered optically thick if it absorbs more than 99% of the excitation (that is, optical density > 2.0).

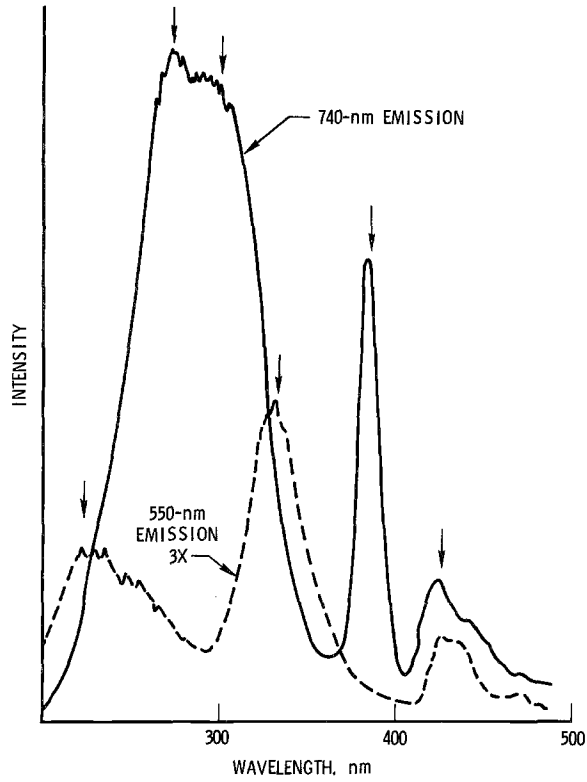

FIG. 4—*Excitation spectra of window glass. These curves show how the intensity of the phosphorescence peaks at 550 and 740 nm depends on the excitation wavelength.*

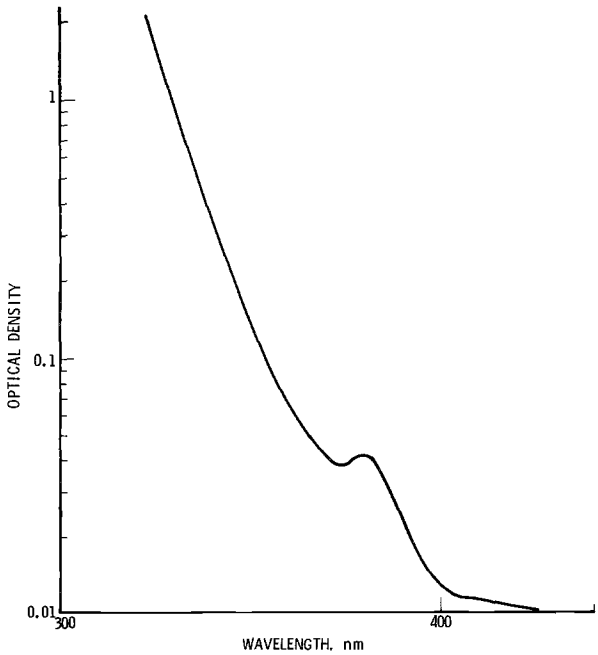

FIG. 5—*Absorption spectrum of window glass.*

in Fig. 4 at the longer wavelengths (325, 385, and 425 nm) will be weaker than the shorter wavelength bands (at 225 and 270 nm) when the sample thickness is reduced. It should be noted, however, that the "bands" that peak at 225 and 270 nm in Fig. 4 are not real but actually reflect the rapidly decreasing intensity of the xenon lamp for wavelengths less than 300 nm.

Comparison of Figs. 4 and 5 provides a dramatic demonstration of the potential of photoluminescence techniques for trace analysis. Although there is no discernible absorption band at 425 nm in Fig. 5, the excitation spectrum in Fig. 4 clearly shows its presence. Similarly, the band at 325 nm is only seen in the excitation spectrum. This latter behavior is typical of the situation where most of the excitation is absorbed by the glass, without luminescence, but a small amount is also absorbed by an impurity with a large luminescence quantum yield.

When the phosphorescence spectra are recorded for the six excitation maxima noted by arrows in Fig. 4, the spectra are generally similar either to those in Fig. 3*a* (observed for 425-, 385-, and 225-nm excitation) or to those in Fig. 3*b* (observed for 325-, 300-, and 270-nm excitation) but with differences in the relative intensities of the two prominent bands. In view of these results, it must be concluded that there are at least four types of phosphorescing species. Excitation at 385 nm preferentially excites species with a phosphorescence that peaks at 725 nm, excitation at 225 and 425 nm preferentially excites species with a phosphorescence that peaks at 540 nm along with the 725-nm band, and excitation at 325 nm preferentially excites species with phosphorescence bands that peak at 575 and 740 nm.

The pronounced decrease in the 580-nm band and the simultaneous increase in the 740-nm band when the excitation wavelength is changed from 325 to 300 or 270 nm indicate that different species are responsible for the phosphorescence bands that peak at 580 and 740 nm. Moreover, it appears that the longer wavelength phosphorescence band is actually composed of two bands, with maxima at approximately 700 and 740 nm, and that the *observed* maximum depends on the relative intensities of these two bands.

The uniqueness of the band that peaks at 580 nm was confirmed by a limited study of the phosphorescence lifetimes. The phosphorescence lifetimes were not measured directly; instead, the changes in the phosphorescence and excitation spectra were monitored as the speed of the phosphoroscope was varied. As the speed of the phosphoroscope was reduced, there was an increasing delay between the time the excitation was stopped and the time the phosphorescence was detected. If the phosphorescence lifetime was comparable to or shorter than the delay time, the phosphorescence decreased as the speed was reduced. However, if the lifetime remained much greater than the delay time, there was no change in the phosphorescence intensity. In this manner, it was found that only the 580-nm band is significantly affected by the phosphoroscope speed (12 000 to 2000 rpm). The lifetime of this band, if an exponential decay law is assumed, is estimated to be 0.3 ms at 77 K. Because the other bands were not affected by the phosphoroscope speed, their lifetimes must be greater than 1.5 ms.

Although all of these observations provide clues to the chemical identity of the emitting species, comparison with the limited studies already published (for entirely different applications) has been fruitless. We are currently performing chemical analyses of our samples in an effort to correlate the phosphorescence analyses with the chemical composition.

Discrimination by Phosphorescent Properties

Most of the 21 glass samples with the same refractive index were found to have different phosphorescence spectra. Although there were variations in the absolute intensities of the phosphorescence bands, as well as changes in the shapes of the bands, this initial study was limited to a simple measure of I_{740}/I_{550}. Clearly, this approach ignores a wealth of data potentially useful for discriminating among samples, but it is faster and simpler than

a detailed comparison of the spectra. It also obviates the need to correct for fluctuations in excitation intensity and precludes problems of reproducible positioning of the sample. For each of the 21 glass samples, the phosphorescence spectra were recorded once for each of the six wavelengths indicated by arrows in Fig. 4. The ratio I_{740}/I_{550} was then measured ten times, with the sample removed and remounted or changed between each measurement. In all cases, at least eight different chips were used. The mean values of the ratios and three times the standard deviation in the mean σ_m are shown in Figs. 6 through 8 for three of the six excitation wavelengths.

Of the six excitation wavelengths used, 425-nm excitation is most useful because it divides the samples into the smallest number of indistinguishable pairs (34 from an original 210) when $\pm 3\sigma_m$ for each glass is considered (Fig. 6). The enhanced discriminating power of the 425-nm excitation data seems to be attributable to a greater precision in measuring I_{740}/I_{550}.[4]

When other excitation wavelengths are used, it is possible to distinguish samples that are not distinguishable by a single excitation wavelength. Thus Samples E, F, and G could not be distinguished with 425-nm excitation but were distinguishable when 270-nm excitation was used (Fig. 7). In Fig. 7, the ratio I_{740}/I_{550} for 425-nm excitation is plotted against the corresponding ratio for 270-nm excitation. This figure shows that when only the data for these two excitation wavelengths are used, the number of indistinguishable pairs is reduced to six. In other words, the group is now separated into 16 distinguishable groups. If the data for the other four excitation wavelengths are also used, it is possible to distinguish all but two pairs of the 21 samples. Thus, as can be seen in Fig. 8, 225-nm excitation makes it possible to distinguish Samples S and Q. This figure also shows a strong correlation for the 225- and 270-nm excitation results. The results for the other excitation wavelengths show similarly strong correlations with either the 270- or 425-nm results. Examination of all the data shows that 270- and 425-nm excitation is the best pair of excitation wavelengths for discrimination among these samples.

The samples used in most of this work were much larger than those generally available in crime investigations. We have shown separately, however, that data with the same

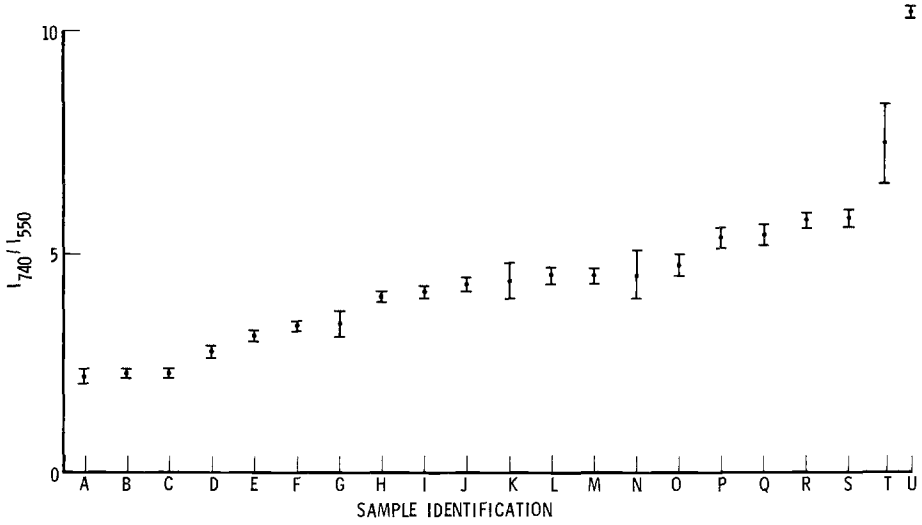

FIG. 6—*Ratio of red to green phosphorescence, 425-nm excitation, for 21 glass samples indistinguishable by their refractive indexes.*

[4]The reason for this greater precision is not obvious, but it may be because this is the only excitation wavelength that maximizes both I_{740} and I_{550}.

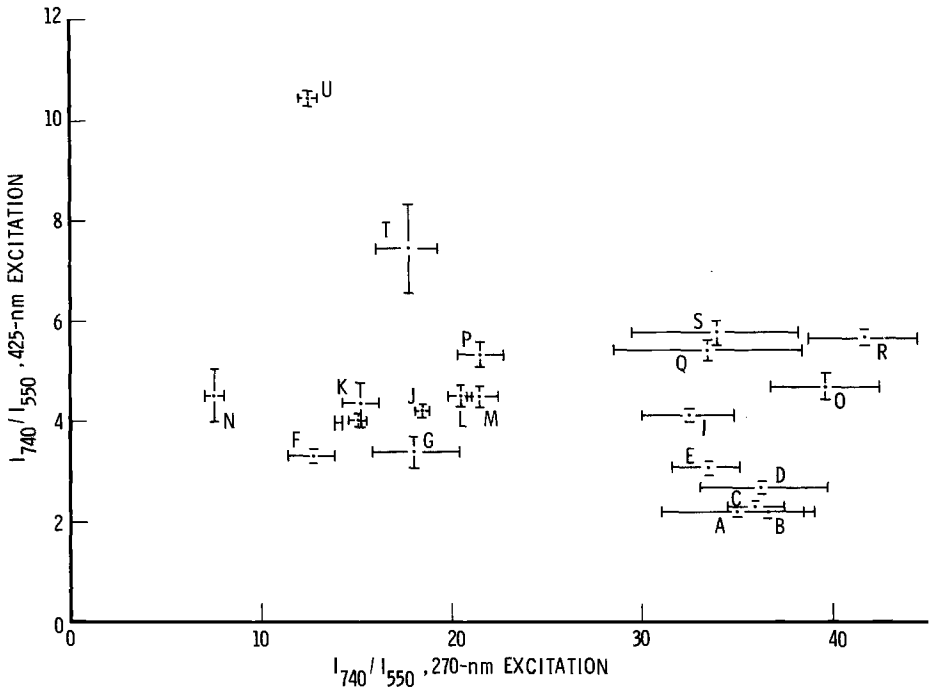

FIG. 7—*Ratio of red to green phosphorescence, 270- and 425-nm excitation.*

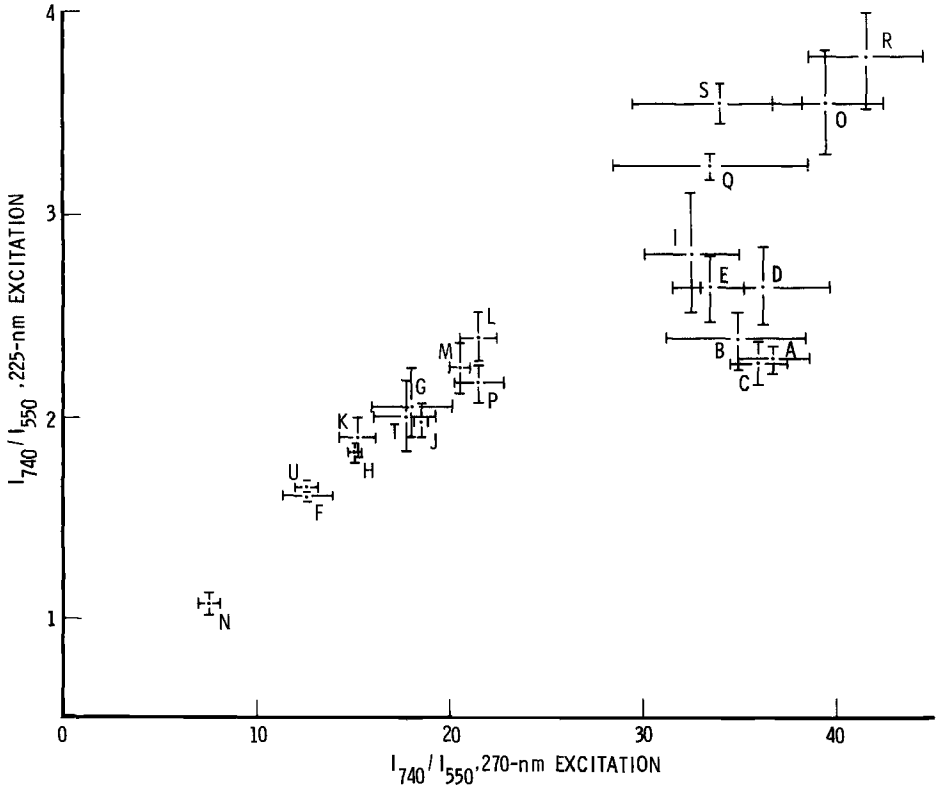

FIG. 8—*Ratio of red to green phosphorescence, 225- and 270-nm excitation.*

signal-to-noise ratio can be obtained for samples as small as 10 mg. With a reduction in the signal-to-noise ratio, samples smaller than 10 mg can be used, but the useful limit for our equipment appears to be 1 mg. If the equipment were modified so that the excitation could be focused to a small spot, it should be possible to use samples even smaller than 1 mg.

An important practical question arises: Within a single window, do the phosphorescent properties vary as they do among samples from different windows? To answer this question, we measured samples from the four corners of two different windows. It was found that different locations within a single window have the same phosphorescent properties, within the precision of the measurements.

Conclusion

The data reported here dramatically demonstrate that discrimination of window glass samples can be enhanced by the use of phosphorescence analysis. There appears to be no significant correlation between the phosphorescent properties and the refractive index; thus, the two can complement each other. Laboratories with the necessary equipment may want to experiment with the current comparison procedure based on I_{740}/I_{550}. If the samples are not too small (≥ 10 mg), the measurements conceivably could be made at room temperature. Although little additional information is gained by the use of more than two excitation wavelengths, the measurements are so rapid and simple that use of all wavelengths, except 300 nm, is recommended.

In view of the relatively simple treatment of the data used in this study, it appears worthwhile to analyze a much larger number of samples and to use the full range of luminescent properties to establish the optimum discrimination capability in quantitative terms. Additional experiments are needed (and some are in progress) to identify the impurities responsible for the phosphorescence and to determine the factors that control the spectral properties of these impurities. In addition, because of the apparent concern for distinguishing window and container glass [*3*] and the difficulty in individualizing headlamp glass, samples of other types of glass should be studied.

Summary

Measurements were made to establish the refractive index distribution of 143 glass samples. These data show that there is a 0.068 probability that two randomly selected window glass samples will have the same refractive index (± 0.0002). Of the largest group of samples that could not be distinguished by their refractive index (1.5166 ± 0.0002), 21 were subjected to phosphorescence analysis. For 17 of the 21 samples, measurement of phosphorescent properties allowed discrimination. The remaining four samples could not be distinguished individually but were revealed as two dissimilar pairs. At least four different species (presumably trace ions as yet unidentified) contribute to the phosphorescence. For all samples, the phosphorescence spectrum consists of two principal bands (with variable intensities) that peak in the green and in the red. The ratios of the intensities of these bands, for various excitation wavelengths, were the only criteria required for discrimination among samples. The measurements, which can be made rapidly without destroying the sample, require samples of at least 1 mg if standard instruments are used.

Acknowledgments

Portions of the data herein were presented to the American Academy of Forensic Sciences at the 27th annual meeting in Chicago, Illinois, February 1975, and at the 29th annual meeting in San Diego, California, February 1977.

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