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Fluorescence Spectrometry in the Identification and Discrimination of Float and Other Surfaces on Window Glasses

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ABSTRACT: Fluorescence spectra have been obtained with conventional spectrometers from glass surfaces varying in area down to 0.05 mm² on fragments as small as 18 µg in mass. In such fragments several fluorescence features can be identified, including the tin fluorescence typical of float surfaces. Float surface fragments may therefore be unambiguously differentiated from other surface fragments by their fluorescence excitation spectra. Thus, in many cases the forensic scientist may now show that the type of glass surface facing the person alleged to have broken it is or is not of the same type as any incriminating fragments. Within the two classes of glass (float and nonfloat) appreciable variation occurs in relative fluorescence intensities. For float glasses there is negligible correlation between the tin fluorescence intensity and any refractive index feature, including the recently reported surface refractive index that is also characteristic of glass of this type.

KEYWORDS: criminalistics, glass, luminescence, fluorescence spectrometry

Because of the recent finding that the surface regions of float glass exhibit refractive indices enhanced relative to the bulk of the glass, float surface fragments may now be identified and differentiated according to origin on the basis of measurements of refractive index [1,2]. The potential evidential importance of this observation follows from the results of Nelson and Revell [3] and of Zoro [4], who have shown that an appreciable proportion of the fragments transferred to a person who breaks a pane of glass are projected at him from the facing surface. Hence, results from fragments present on the clothing of a suspect in a breaking and entering case, for instance, may now be checked for consistency with whether or not a particular float glass surface was facing him when he broke it. However, a dual refractive index effect cannot invariably be characterized in float glass fragments unless they are crushed and therefore destroyed prior to examination [2], the measurements are difficult and time-consuming to make [1], and the possibility of variation in refractive index within a single fragment gives rise to ambiguity in the interpretation of such measurements on occasion [4]. Indeed, there is no reason to suppose that other sources of a similar variation could not occur. It is therefore important that an alternative test for float surfaces on small fragments of glass be found.

When irradiated with ultraviolet (UV) light many glasses fluoresce, and by visual in-

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spection of the fluorescence different glasses may be distinguished from one another [5]. Some early forensic science applications have been reviewed [5,6]. The fluorescence is due in part to a variety of heavy metal ions [7], one of which is tin, when shortwave UV excitation (for example, the 254-nm mercury line) is used. The fluorescence attributed to the tin that occurs at high concentrations in the surface regions of float glass [8] is commonly used as a diagnostic visual test for glass of this sort, but any evidential application of the effect is restricted by the difficulty with which the relative fluorescence intensities from small fragments of glass can be visually assessed. Under the test conditions all glass surfaces are effectively fluorescent relative to the bulk glass (with 254-nm excitation the fluorescence emission is localized at the sample's surface by the opacity of the glass in this wavelength region), and therefore the identification of a surface-derived fragment as float glass or other glass must rest on a subjective comparison of the fluorescence from any remaining planar surface with that from fracture surfaces. In apparent intensity the latter fluorescence is highly sensitive to the detailed shape of the fragment.

Although at the outset of this work there appeared to be little prospect of the ready adaptation of presently available fluorescence spectrometric techniques to the examination of small fragments in the wavelength regions of interest, it seemed that a spectrometric characterization even of the larger pieces of glass typical of control samples might be of use. Whether or not the varying refractive index effect should be sought or expected in a case would therefore depend on an objective record, rather than on a subjective observation and the less certain conclusions attending it as at present; an improved understanding of the nature of the fluorescence would facilitate the development of techniques appropriate to small fragments; and the spectrometric results might provide independent evidence bearing on the conclusions drawn [1,2] from the refractive index results. In the outcome, small fragments of glass may now be spectrometrically characterized.

Apart from the fluorescence, the photoluminescence of glass contains phosphorescence that has been effectively used by Calloway and Jones [9] in the discrimination of glasses. Phosphorometric techniques enable some of the problems encountered in fluorometric work on solids to be avoided. However, the luminescence characteristic of float glass is a relatively prompt emission and must be treated as fluorescence for the purpose of its measurement. (For discussion of other pertinent analytical techniques see Ref 9.)

Experimental Procedure

The results were obtained with Baird Atomic SF-100E and Perkin-Elmer MPF-4 fluorescence spectrometers. The former instrument was fitted with doubled monochromators on both the excitation and the emission side, whereas single monochromators were fitted in the latter, which is more subject to the effects of stray light.

For the initial work on larger pieces of glass, done on the SF-100E, the glass was clamped across the instrument's cuvette holder with two spring clips so that the intersection of the excitation and emission axes coincided with the glass surface. The angle of incidence of the excitation was 45°. To remove all stray light and excitation reflected from the sample's surface at wavelengths less than 400 nm, a 1-cm cuvette containing a solution of 2.5 g of sodium nitrite in 7.5 g of water was mounted between the sample and the emission monochromator. The slit widths were set to give a band pass of 5 nm for whichever monochromator was being scanned, and 15 nm for the other. Under these conditions the area of the sample excited was 0.3 cm².

For measurements on deliberately restricted ("masked") surfaces or on small fragments an attachment (Fig. 1) that fits into the SF-100E cuvette holder was used. Part A (Fig. 1) is a cuvette spacer ground down so that the excitation-emission intersection falls across a 2-mm-diameter hole B (the sample position) drilled in the metal plate C. The position of C on A is adjusted to give a maximum fluorescence response when a strongly fluorescent

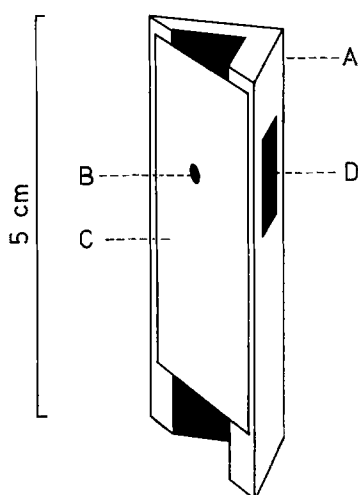


FIG. 1—Perspective diagram of the sample holder: A is a modified cuvette spacer; B is a 2-mm-diameter hole drilled in the metal plate C (0.4 mm thick); and D is the exit aperture of the emitted fluorescence. Excitation enters through the aperture similar to D in the back face of the holder. The long dimension of the holder is 5 cm.

sample (a fluorescent-whitened self-adhesive label) is fixed across B; the final adjustment is made while the Araldite (Ciba-Geigy, Cambridge, United Kingdom) used to hold C on A is setting. The whole assembly is coated with matte black paint.

The heights of the excitation and emission slits in the spectrometer's sample compartment are reduced with black insulating tape to suppress as far as possible any fluorescence or scattered light from areas outside the sample area. Otherwise the slit widths and the filter are the same as for the larger samples. Samples with a surface area greater than B, that is, $>3 \text{ mm}^2$, are clamped across B with a spring clip or held in place with a mountant ("Black Tac") made by kneading carbon black ("Sevacarb MT," Sevalco, Bristol, United Kingdom) into "Blue Tac" (Bostik, Leicester, United Kingdom) up to the point where the mixture becomes fairly resilient and no further blackening is possible. Small fragments of glass are mounted in the Black Tac directly. A ball of the mountant, about 1 cm diameter, is partly flattened onto a piece of filter paper that has been liberally dusted with carbon black. The resulting matte area of the mountant is then pressed onto the fragment, which has been set with its plane surface in contact with a microscope slide. Usually at this point interference colors (parallel bands) can be seen if the surface of the fragment is viewed under magnification through the slide. This corroborates the presence of a plane surface on the fragment. The mountant with the adhering fragment is removed from the slide, reflattened on a clean slide if necessary, and then stuck onto the plate C of the sample holder so that the fragment is centered on the hole B but does not intrude into it.

Samples are presented to the MPF-4 spectrometer in a similar way, on a drilled metal plate fixed to the instrument's solid sample accessory. The angle of incidence of the excitation is 30° . The alignment of the sample position is done as before, and the heights of the excitation and emission beams are again restricted. Because the excitation beam is sharply focused on the sample position in this instrument, which results in a critical dependence of the measured spectra on the sample's alignment, the slit image at the sample position is deliberately thrown slightly out of focus by an adjustment of the excitation lens in the sample compartment. The instrument's stray light level necessitates the use of a filter in

the excitation beam to remove stray light in the visible region; light below 230 nm is also removed by the filter used. On the emission side are inserted the instrument's cut-off filters up to within 10 nm of the shortwave edge of the region monitored. Band passes are usually set at 5 nm (for scanning) and 10 nm (monitoring).

Prior to their being examined, large pieces of glass are washed in acetone and water and rubbed dry with a lens tissue. Small pieces and fragments are washed in chloroform, with sonication if adherent debris is present, and dried.

Results and Discussion

Some Spectrometric Considerations

Fluorescence spectrometers are commonly designed for the examination of solutions with perpendicular illumination, when the cuvette geometry can be fairly closely defined and the parts of the cuvette and its holder lying in the excitation beam are not viewed by the detector. The amount of stray light and excitation passing through to the detector is therefore minimized. In the examination of solids, with frontal illumination, high levels of stray light and excitation are deflected to the detector and must be removed before any fluorescence can be measured. Of the two spectrometers used the stray light level was expectedly much less in the doubled monochromator instrument, which proved to be the most useful therefore, but to obtain spectra adequately free from spurious detail, such as that caused by the spectrometers' xenon source lamps, it was necessary to use filters in both cases. The use of polarizers yielded no improvement over the described technique.

All of the spectra presented are uncorrected. Consequently, the excitation spectra are a convolution of the spectral characteristics of the samples with the spectral outputs of the spectrometers' sources and the characteristics of the excitation monochromators. Smaller effects influence the emission spectra. In view of the variety of other factors to which the spectra are subject (some of which are mentioned below), it is doubtful whether any effective correction of the spectra could be made. But the results from any one spectrometer should be internally consistent, and the main results of this work have been deliberately duplicated on two very different spectrometers.

In the 250- to 260-nm region, which is generally used for excitation in the visual detection of float surfaces, the absorbance of soda-lime glass is on the order of 60 per cm (from experiments with blown glass films), and for most purposes the glass might be considered to be quite opaque, with its fluorescence localized at the surface. Even so, the depth of glass required to reduce the intensity of the excitation by half, about 50 μm , evidently exceeds the depth penetrated by the tin. By microscopy it can be seen that most of the characteristic fluorescence of irradiated (254 nm) cross sections of float glass occurs down to an approximately 10- μm depth, which is comparable to Underhill's results from refractive index measurements [1] and to the results from other techniques [10] for the depth of tin. Hence, fluorescence from below the tin-containing region will be excited to an extent varying as the effective depth of the sample is varied by its wavelength-dependent absorbance. An actual surface can exhibit no fluorescence, or refractive index for that matter. Both require a finite volume for their observation.

The full depth of a sample will be excited in the near-UV range, where glass is transparent. If the sample's size is not a limiting factor, its effective depth, and hence the proportion of bulk to "surface" fluorescence seen, will be controlled by the spectrometer's slit widths, by any mask applied to the sample's surface (as in the sample holder in Fig. 1), and by the orientation of the surface with respect to the excitation and emission axes.

The intervention of some of the foregoing effects is illustrated below, and most of these effects were encountered. But their influence is small within the bounds of the conclusions

drawn. Attention is directed to them here because they must be taken into account in the interpretation of any results from different experimental arrangements.

Spectral Characteristics of the Fluorescence

In Fig. 2 are shown fluorescence spectra taken from a typical float surface with the doubled monochromator spectrometer (SF100-E). The main emission is a very broad band with a maximum at about 490 nm. The corresponding excitation is at 280 nm, under the conditions used. Another excitation appears in the 260-nm region and produces a second emission superimposed on the first to give an envelope truncated in the 400- to 420-nm region by the sodium nitrite filter used to remove stray light. A third excitation occurs at 340 nm, with the corresponding emission again truncated. Other experiments made with the MPF-4 indicate that this last emission peaks at 375 nm.

Spectra from the nonfloat surface of the sample used for Fig. 2 are shown in Fig. 3, where the lowermost pairs of spectra were run at the same sensitivity as before (Fig. 2). Similar spectra are obtained from sheet glass surfaces. Only one strong fluorescence is present, with an excitation at 340 nm and a corresponding emission as in the float surface, and of similar intensity. This, then, is referred to as the "bulk" fluorescence. On excitation at 280 nm an emission closely comparable to the major float surface emission is seen, but at 15% of the latter's intensity. Evidently the emissions from the two surfaces are qualitatively undifferentiated. Although on visual inspection the two surfaces of a piece of float glass are clearly distinguishable because of the difference in intensity, if only one surface is available (as in a broken fragment) float and nonfloat surfaces could be confused, particularly in view of the considerable variation in intensity that occurs between different samples of float glass. However, the two surfaces are clearly qualitatively differentiated in their excitation spectra. For example, the excitation spectrum of the non-

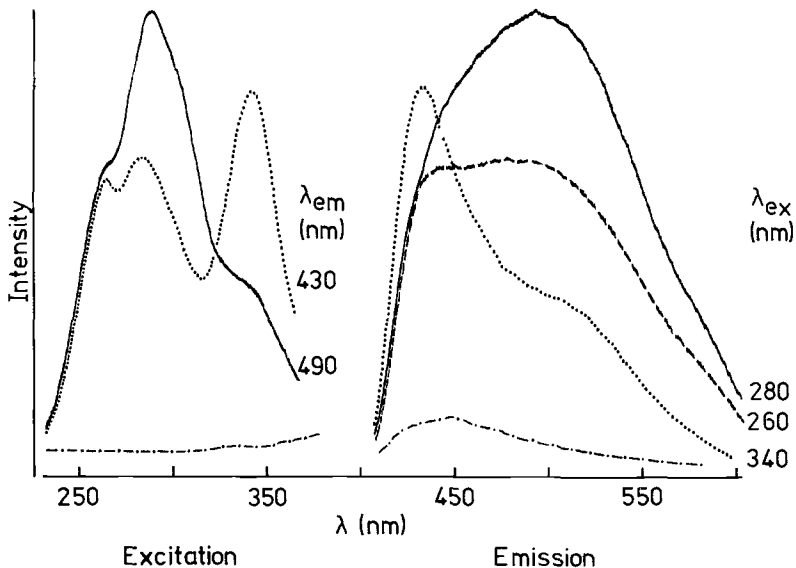


FIG. 2—Excitation and emission spectra (spectrometer, Baird Atomic SF-100E) of a float glass surface, 0.3 cm² in area. The "Morse code" lines are excitation and emission spectra of a Spectrosil quartz plate (monitored at 490 and 280 nm), run as a blank with unaltered sensitivity settings.

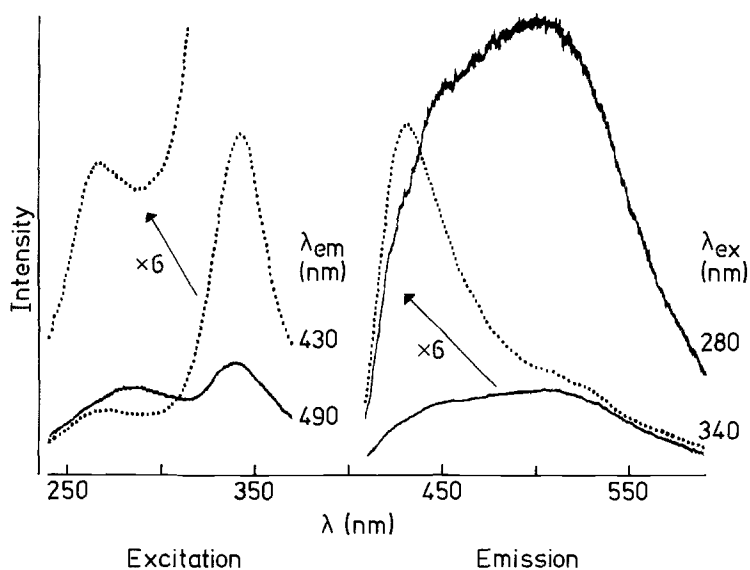


FIG. 3—Excitation and emission spectra of a nonfloat surface; the conditions were the same as those of Fig. 2 except that relative sensitivities were varied as indicated.

float surface monitored at 430 nm (Fig. 3) shows neither of the resolved excitations at 280 and 260 nm of the float surface (Fig. 2). The same result was obtained from each of 36 other samples of float glass, kindly made available by Dr. R. J. Dudley. In no case has there been any possibility of confusion between float and nonfloat surfaces either in this set of samples or in any other window glass examined to date.

Origin of Float Surface Fluorescence

The excitation at 280 nm (Fig. 2) results, as expected, from tin. Figure 4 shows spectra obtained from a glass made by the fusion of sodium silicate to which stannous chloride had been added onto a Spectrosil silica plate. These spectra clearly correspond to the main excitation and emission features present in the float glass spectra included in Fig. 4. The same result was obtained from a sodium silicate glass incorporating stannic oxide; hence, the oxidation state of the tin must be altered during the experiment. Both stannous and stannic tin may occur in float glass [8]. In cryogenic glasses only stannic tin fluoresces [11], but in inorganic phosphors only stannous tin functions as an activator [12]. Other metals that gave fluorescent sodium silicate glasses included arsenic, bismuth, cerium, copper, lead, antimony, thallium, and zinc. The arsenic, lead, and antimony excitations occurred in the 250- to 280-nm region with emission maxima in the near UV, but whether any of these or different tin species is responsible for the 260-nm excitation (Fig. 2) remains undecided. It would clearly be of interest to examine the fluorescence of heavy metals in glasses corresponding in composition more closely to window glass, in particular, to unambiguously determine the fluorescence characteristics of the two oxidation states of tin. (That these results are from uncorrected spectra, as mentioned before, cannot be too strongly emphasized here; the quoted wavelengths are undoubtedly extensively red-shifted from their real values. Their significance is entirely comparative.)

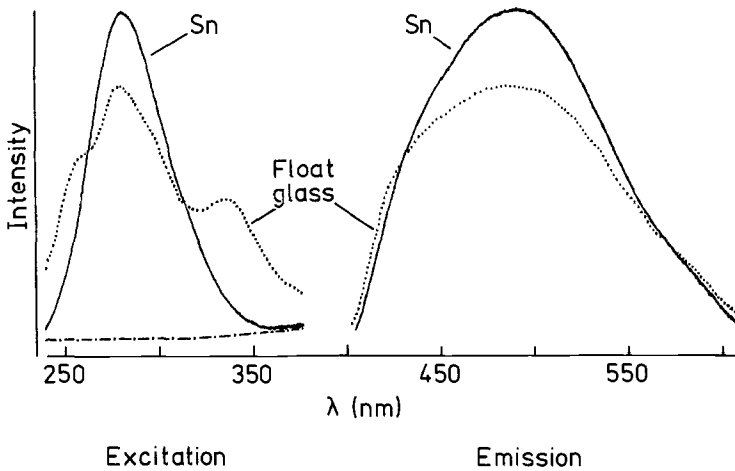


FIG. 4—Excitation and emission spectra of a sodium silicate glass containing tin and of a float glass surface. The "Morse code" line is a sodium silicate blank.

Differences Between Spectra from Different Spectrometers

In Fig. 5 are shown excitation spectra from both surfaces of a float glass recorded with the MPF-4 (single monochromators instrument) and monitored at 400 and 500 nm. These wavelengths enhance the tin and the bulk excitations individually and were selected to display as far as possible the excitations shown in Figs. 2 and 3 from the SF-100E (doubled monochromators). The differences in the monitoring wavelengths from those used for Figs. 2 and 3 (430 and 490 nm) are necessitated by the different experimental arrangement, but the same excitations are revealed, although they are less well resolved and the long-wave excitation is shifted down to 325 nm. The two instruments produce similar emission spectra, but the effects of stray and scattered light are more pronounced in spectra from the MPF-4. The long-term stability of the spectra is easier to maintain in the MPF-4, in which most of the optics are sealed against the laboratory atmosphere, but in either case all comparisons between samples have been made with reference to a standard glass.

Variation over a Window Pane

From ten evenly distributed points on a 35- by 35-cm pane of float glass were taken pieces of about 10 cm², and the excitation spectra, monitored at 460 nm, of both surfaces of each piece were recorded on the SF100-E spectrometer. The effective area of the samples excited was 0.3 cm². On the following day the samples were run again in random order. At intervals during both days spectra of a single piece of another float glass were run as a standard. The intensities above the spectrometer baseline were measured in arbitrary units at 280 and 340 nm, which correspond to the principal emissions monitored at 430 nm in Fig. 2. (The longer monitoring wavelength intensifies the tin excitation at the expense of the excitation in the 260-nm region, which was not used here.) A drift of 13% in instrumental sensitivity over the two days was evident in the standard's spectra, for which the results were corrected with reference to the standard. The results from an analysis of variance are given in Table 1. Variance ratios greater than 6.2 are significant at the 5% level.

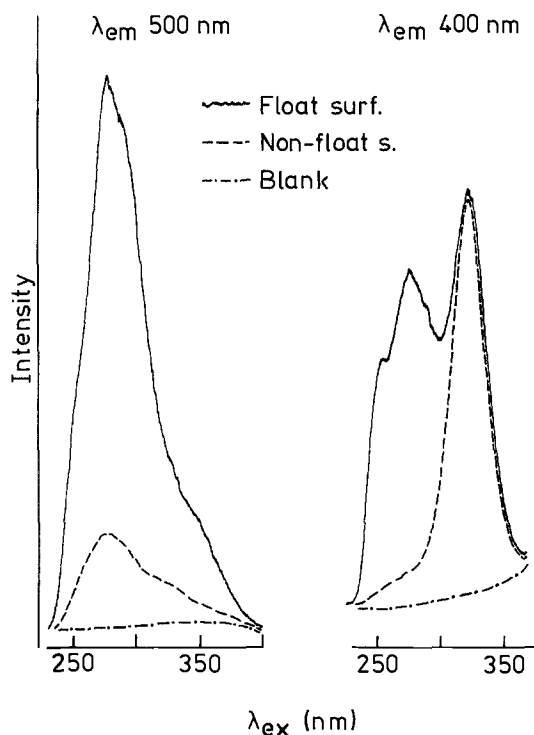


FIG. 5—Excitation spectra from the Perkin-Elmer MPF-4, with the indicated monitoring wavelengths, of the two surfaces of a float glass. The blanks are Spectrosil quartz. All the spectra were run at the same sensitivity. The sample area is 0.03 cm^2 in each case.

Evidently the bulk fluorescence, but not the tin fluorescence, varied significantly, which must be taken into consideration in any evidential use of the former. Some further results relevant to within-sample variation are given below.

Bleaching

Under strong UV irradiation glass fluorescence is subject to bleaching. Thus, a sample irradiated at 250 nm for 5 h in the sample compartment of the MPF-4 spectrometer, at maximum slit widths, exhibited a fall in the fluorescence excited in this region of about 10%. At 320 nm a 25% reduction occurred. When the samples were reexamined a month later the fluorescence intensities had partly reverted to the original values. It is conceivable that the effect could give rise to within- and between-sample variation, but under usual circumstances this seems unlikely and has not been detected. If the effect was important, then considerable variation between the two surfaces of nonfloat panes would occur because a directly sunlit surface, for example, would be subject to very much higher levels of UV light than its opposed surface because of the absorbance of UV by the intervening glass. However, in a set of 35 samples of nonfloat window glass collected at scenes of crime no significant variation between the two surfaces of any sample was found. This study should have been particularly revealing because the nonfloat (bulk) fluorescence is evidently the most susceptible to the bleaching effect. The main consequences of the effect are that samples of any glass used as a standard must be regularly checked for fading against

TABLE 1—Variation of fluorescence intensity over a pane of float glass.

Statistic	Intensity ^a			
	Float Surface		Nonfloat Surface	
	280 nm	340 nm	280 nm	340 nm
Mean	119.1	73.6	27.9	68.8
Within-sample SD ^b	1.9	1.4	1.2	2.0
Between-sample SD	3.0	3.6	1.3	4.7
Variance ratio (9/10 d.f. ^c)	2.5	6.6	1.2	5.5

^aThe intensities are relative to a standard sample of float glass at the indicated excitation wavelengths. The monitoring emission wavelength was 450 nm. The sample surface area excited was 0.3 cm².

^bStandard deviation.

^cDegrees of freedom.

other samples of the same standard and that the future application of very bright sources of excitation, such as lasers, may be restricted.

Correlation with Refractive Index Measurements

Presumably, the surface refractive index effect is due to the tin content of the surface layers of float glasses [1.2]; therefore, it might be expected that the ΔRI values (differences between bulk and surface refractive indices) of Davies et al [2] would be correlated with the tin fluorescence intensity values. The values obtained by Davies et al (who generously made their data available) from collections of window and toughened (automobile) float glasses are plotted in the scatter diagram of Fig. 6. For consistency among the fluorescence intensity data, all of the samples were mounted on the holder shown in Fig. 1, and both sets of intensity values are relative to the same standard.

Obviously (Fig. 6), any correlation is small. For the window glasses the coefficient is 0.50, which is just above the 5% level (0.48) tested against 0. For the toughened glasses the coefficient is 0.21, and for the two sets of data combined, 0.29. There is no other coefficient significantly different from 0 between any of the other fluorescence and refractive index features.

These results show that ΔRI and the fluorescence intensity values cannot both be directly related to the concentration of tin. As the effective optical depth of the glass significantly exceeds the tin depth, the results are not likely to be much influenced by any differences between samples in the concentration gradient or in the depth of the tin. The most probable explanation is the occurrence of the tin in more than one form, for example, the previously mentioned two oxidation states. This being so, it is now possible to apply the differences in the ratio of a metal's oxidation states to the discrimination of fragments of glass.

Variation Between Window Glasses

Considerable variation occurs between the fluorescence intensities of different samples of float glass and, to some extent, nonfloat glass. Table 2 shows data from an analysis of variance of the fluorescence of 31 samples of float window glass. These data include the previously mentioned sample set and other samples from scenes of crime. The measurements were made on unmasked surfaces (0.3 cm²), with the fluorescence emission monitored at 460 nm. Duplicate analyses were made on different pieces from each sample

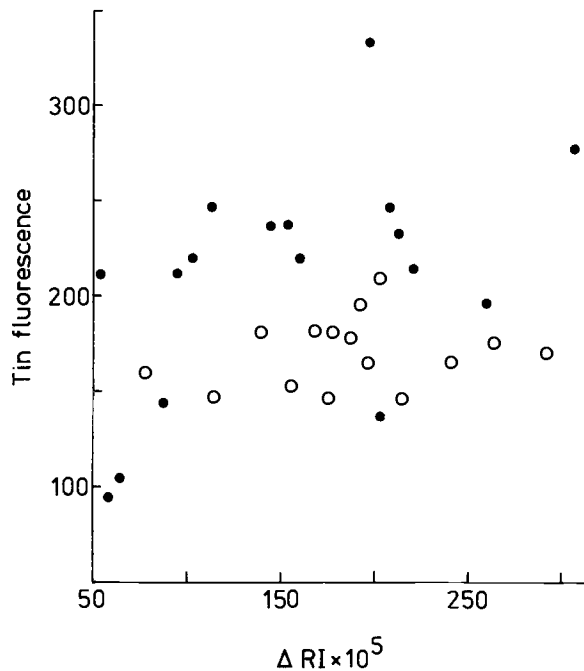


FIG. 6—Distribution of the tin fluorescence intensity of window float glasses (solid circles) and toughened (automobile) float glasses (open circles) with respect to ΔRI .

TABLE 2—Variation of fluorescence intensities in a collection of 31 float window glasses.

Statistic	Intensity ^a			
	Float Surface		Nonfloat Surface	
	280 nm	340 nm	280 nm	340 nm
Mean	204.6	68.1	27.7	59.0
Within-sample SD	5.0	3.0	1.3	2.3
Between-sample SD	104.6	26.4	4.8	26.9
Variance ratio (30/26 d.f.)	438	77	14	137

^aSee footnotes to Table 1.

when these were available, so that any variation across an area of breakage contributes to the within-sample variation. The principal variation between samples lies in the tin fluorescence (the actual variation between the highest and the lowest samples was by a factor of 3.6), although the bulk fluorescence (340 nm) also varies significantly. In a collection of 19 nonfloat glasses, from scenes of crime, the variance ratio for the bulk fluorescence was 238.

For the float glass samples, Table 3 shows the discriminating power [13-15] of the various features taken individually and in combination on the assumption that a pair of samples is discriminated when the range of results for any one feature exceeds the upper 5% point of the "Studentized" range [16]. The bulk refractive indices are included in the table. The standard deviations used in the calculation of the ranges are from Table 2

TABLE 3—Discriminating powers of various features, singly and combined, in a collection of 31 float window glasses.

Bulk Refractive Index	Fluorescence Intensities			
	Float Surface		Nonfloat Surface	
	280 nm	340 nm	280 nm	340 nm
0.935	0.983	0.908	0.454	0.834
		0.959	0.873	
		0.991	0.978	
		0.993		
			0.783	

and from the refractive index data of Davies et al [2]. A high level of discrimination is afforded by the tin fluorescence alone, and this is enhanced appreciably when combined with the bulk fluorescence and the bulk refractive index.

From their lack of correlation with the fluorescence results, the ΔRI values offer further discrimination. For the samples of Table 3, for which data are available [2], the combination of bulk and ΔRI values gives a discriminating power of 1.0, and hence no further discrimination is possible from fluorescence measurements. But the tin fluorescence alone gives a discriminating power of 0.912, and all the fluorescence features combined give 0.993 and a value of 1.0 in combination with the bulk refractive index.

The discriminating power of ΔRI and fluorescence measurements was compared in a collection of seven float glasses poorly differentiated by bulk refractive index: the results fall in the range 1.51716 to 1.51726. The fluorescence of the samples varies considerably, as shown in Fig. 7, where spectra from the extremes and the middle of the range of the samples are compared. Solely on the basis of the tin fluorescence the discriminating power is 0.952. Only 1 out of 21 pairs of samples is not separated. Discrimination in terms of ΔRI was made difficult by the wide variation found in the within-sample standard deviation, which was therefore estimated for the samples individually. The comparisons were made at the 95% level (t distribution) threshold appropriate to each pair. The discriminating power is 0.81: four pairs are not differentiated, but these do not include the pair undifferentiated in fluorescence. Hence, if the two sets of results are taken together the differentiation is complete.

Application to Small Surfaces

The technique of restricting the area of surface excited by a mask (the drilled plate C in Fig. 1) to 0.03 cm^2 enables surfaces of this size and smaller to be characterized. Apart from the increased instrumental sensitivity required, which has never been a limiting factor, the main effect on the spectra derives from the consequent reduction in the optical depth of the sample: the contribution of the bulk fluorescence to the spectra is reduced. An example is given in Fig. 8. The effect can be offset if the monitoring emission wavelength is moved to 430 nm, which also increases the resolution of the shortwave UV band that otherwise is usually seen only as a shoulder on the main tin fluorescence. This provides another discriminating feature, as the spectrum from the second sample in Fig. 8 shows. If the results are referred to the same standard at the same monitoring wavelength, the relative fluorescence is little changed from that of the unrestricted surfaces. Thus, for the collection of 17 float glasses the mean relative tin fluorescences are 216 and 210 for 0.3- and 0.03-cm^2 surfaces, respectively; the correlation coefficient between the two sets of

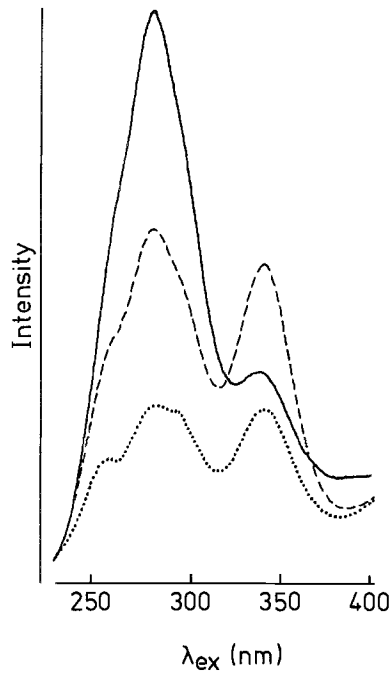


FIG. 7—Excitation spectra, monitored at 460 nm (SF-100E), of three samples of float glass undifferentiated in bulk refractive index. All the spectra were run at the same sensitivity setting and refer to sample areas of 0.3 cm².

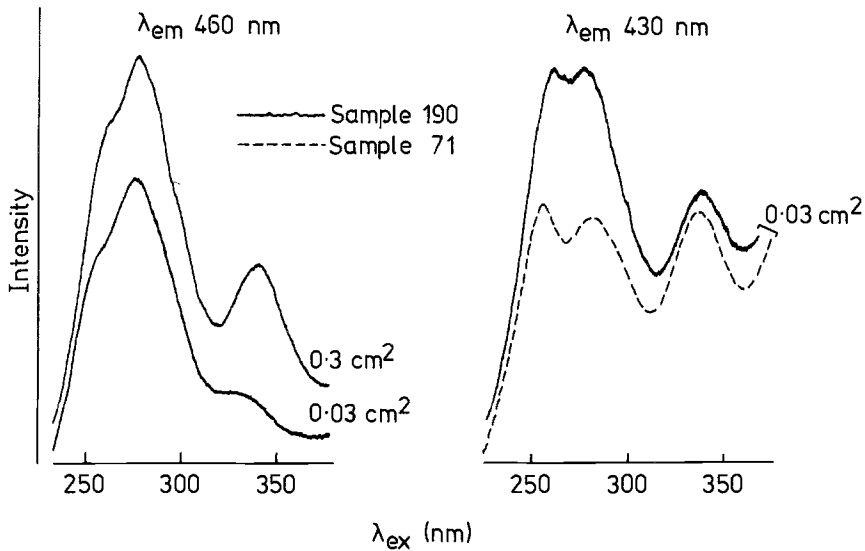


FIG. 8—Excitation spectra of unmasked (0.3 cm²) and masked (0.03 cm²) surfaces monitored at 460 and 430 nm (SF-100E). In the latter, different samples are compared. Sensitivity settings were arbitrarily varied.

results is 0.991; and the discriminating powers are 0.912 and 0.890, corresponding to an additional three pairs undifferentiated in the latter case. Among the seven float glasses similar in bulk refractive index the discrimination is unaltered.

Toughened Glass Fragments

Provided that the sample surface entirely covers the sample hole in the mask and that an appreciable depth of uncracked glass is present (for example, the two-surfaced fragments typical of broken toughened windshields), the spectra do not depend significantly on the size of the fragment. Thus, for 20 fragments from one windshield, with float surfaces present varying between 1.0 and 0.04 cm² and having a mean value for the relative tin fluorescence of 157, the between-fragment standard deviation was 3.2, and within-fragment, 2.1. (To obtain the latter value, fragments were reorientated an average of 3.5 times on the sample holder.) It is also evident from these results that any variation in tin fluorescence between different points on the windshield was small.

Table 4 presents data showing the between- and within-sample variation in fluorescence in a collection of 29 toughened float glass samples. These include the 20 samples used by Davies et al [2] and a further nine samples collected locally. The data refer only to the float surface and include the excitation at 260 nm. For each feature the between-sample variation is highly significant. In the order given in Table 4, the discriminating powers of the three features individually were found to be 0.547, 0.731, and 0.796. From the features taken together the result was 0.958; out of 406 pairs of samples, 17 were not discriminated.

For 15 of the samples ΔRI values are available [2]. Under the discrimination criteria used here, the discriminating powers of the bulk refractive index and ΔRI are 0.876 and 0.867, respectively, and 1.0 when the two are combined. The combined fluorescence features yield 0.962 and, in conjunction with bulk refractive index or with ΔRI , 1.0 or 0.990.

Apart from the negligible correlation between ΔRI and tin fluorescence already demonstrated in Fig. 6, the intensity and the between-sample variation of the tin fluorescence of toughened glass are both reduced in comparison to window glass (Tables 2 and 4). Even so, a useful degree of discrimination remains, and the technique is readily applied to the size of fragment commonly encountered in case work. The reduced intensity may be due to the oxidation of stannous to stannic tin that occurs during toughening [8], if the fluorescent state is the former.

Small Fragments of Glass

The main factors limiting the characterization of samples with very small plane surfaces are the alignment of the surface in the spectrometer, the low level of the sample's fluorescence relative to the level of other sources of detected light, and whether or not a plane surface is being examined. The latter point can generally be decided by direct visual examination of the reflectivity of the surface, but the technique described usually enables the presence of an aligned plane surface to be confirmed although not to be definitely excluded—the interference effect is not invariably seen with known surface fragments. As the interior of the sample holder is subject to very high levels of light its matte surface must be carefully maintained to minimize the effects of any background fluorescence and scattered stray light. Similarly, the surface of the mountant must carry a fresh dusting of carbon black.

The present lower limit of surface area that can be characterized as float glass or non-float glass is in the region of 0.1 mm², such as might occur on a fragment of about 50 μg . In Fig. 9 are shown spectra from a large piece of float glass that completely covered the sample hole (3 mm²) in the holder and fragments of the same glass with plane surfaces of 0.29 and 0.12 mm² (estimated from the surface dimensions measured by microscopy), to-

TABLE 4—Variation in relative fluorescence intensities in a collection of 29 toughened (automobile) float glasses.

Statistic	Intensity ^a (Float Surface)		
	260 nm	280 nm	340 nm
Mean	13.1	145.8	79.2
Within-sample SD	1.9	3.4	3.0
Between-sample SD	7.5	28.1	26.9
Variance ratio (28/27 d.f.)	16	68	80

^aFrom 0.03-cm² surface, relative to a standard sample of float glass at the indicated excitation wavelengths. The monitoring emission wavelength was 430 nm. The 280- and 340-nm intensities were taken from the spectrometer baseline. The 260-nm intensity was defined as (relative intensity at 280 nm) - (relative intensity at 260 nm) + 10.

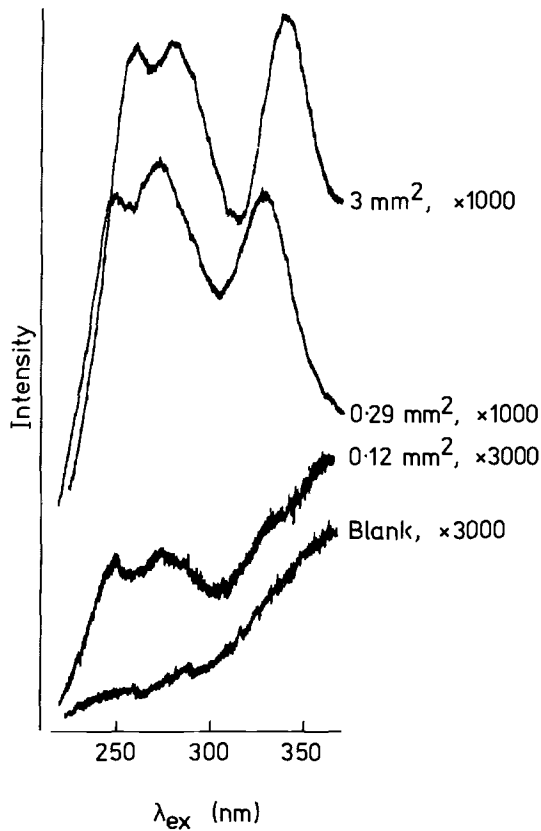


FIG. 9—Excitation spectra monitored at 430 nm (SF-100E) from a masked (3-mm²) piece of float glass and from float surfaces remaining on broken fragments of the same glass, at the indicated sensitivities. For the blank, the sample hole (Fig. 1) was filled with Black Tac.

gether with a blank from the mountant. The smaller fragment weighed $63 \mu\text{g}$. The decrease in the bulk fluorescence relative to the tin fluorescence as the sample size, and hence depth, decreases is apparent in the spectra, but the presence of the float surface is unambiguously shown by the two maxima in the 250- to 275-nm region. Although these are shortwave-shifted relative to those of the larger surface, because of the reduced sample depth, their appearance is unmistakable. For comparison see Fig. 10, where spectra from small nonfloat surfaces are shown. No excitation peak in the 275-nm region is present at all. From Fig. 9 one further point is apparent: fluorescence intensity may decrease neither as rapidly as nor regularly with the surface area. In a small fragment the nonirradiated surfaces close to the irradiated surface can act as reflectors, which increases the fluorescence detected.

The minimum sample size is further reduced when the spectra are monitored at longer wavelengths, where the signal resulting from the background is less and the tin fluorescence is increased. In this way, spectra may be obtained from surface areas down to 0.05 mm^2 (Fig. 11). The mass of this fragment was $18 \mu\text{g}$. The resolution seen in the shortwave region is reduced so that some loss in selectivity occurs, but sufficient resolution remains to enable the fragment to be identified as from a float surface.

Although with very small fragments the loss of the bulk fluorescence prevents direct comparison between spectral patterns of different float glasses, this comparison can still be made with relatively small fragments. For example, Fig. 12 compares spectra from 3-mm^2 surfaces of two "control" pieces of float glass, of the same bulk refractive index, and fragments from them of 0.4-mm^2 plane surface area. Despite the spectral changes that have occurred, the two fragments are still clearly differentiated and assignable to their parent samples.

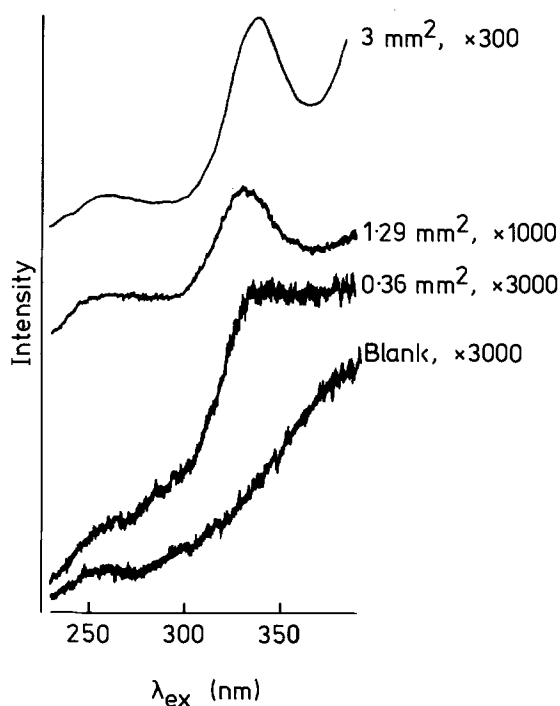


FIG. 10—Excitation spectra of a nonfloat surface and fragments. Other relevant details are as given in Fig. 9.

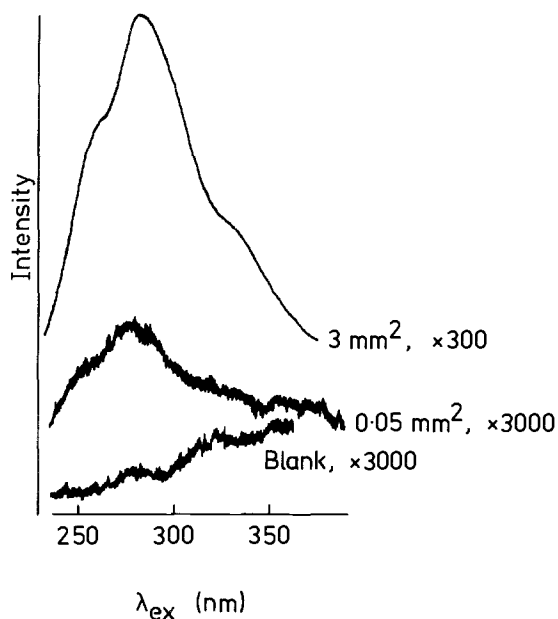


FIG. 11—Excitation spectra, monitored at 488 nm (SF-100E), of a float surface and a fragment from it. Other details are as in Fig. 9. The mass of this fragment was 18 μ g.

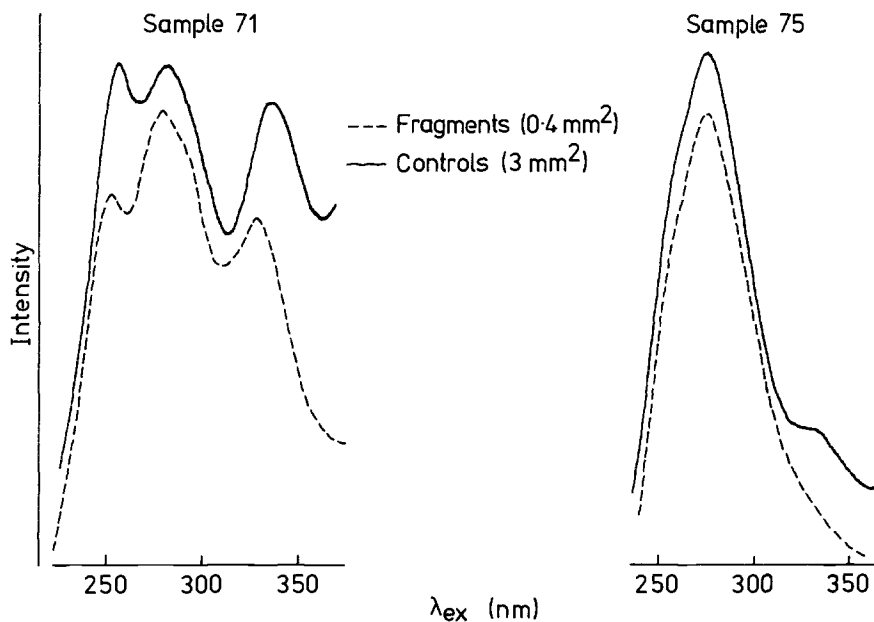


FIG. 12—Excitation spectra, monitored at 430 nm (SF-100E), of a "control" masked piece (3 mm²) and a fragment (0.4 mm²) of each of two float glass surfaces. The bulk refractive indices of the two samples were indistinguishable. The instrumental sensitivity was arbitrarily varied.

These results were obtained with the doubled grating spectrometer (SF100-E). However, provided that the experimental conditions are optimized, comparable results should be obtained with other instruments. In the case of the optically very different MPF-4, for instance, similarly small sample sizes may be dealt with just as readily. Examples from a float and a nonfloat surface (0.18 and 0.17 mm², respectively) of the same glass as shown in Fig. 5 are shown in Fig. 13. The spectra are monitored at two emission wavelengths, 400 and 500 nm, for the reasons mentioned before. The two surfaces are clearly distinguishable and display the same features present in the spectra from the larger sample (Fig. 5).

The question may be raised whether the presence of tin in the bulk of a glass might vitiate attempts to distinguish float from nonfloat surfaces when only one original surface is present. For instance, the tin might be introduced in a float glass cullet. However, the redistribution of "surface" tin, 10 μm in depth, throughout the bulk of a glass, say 5 mm, would reduce its concentration by a factor of 0.002, and its fluorescence would not be observable. (To confirm a localized tin distribution, a float surface fragment may be turned back-to-front in the spectrometer when little tin fluorescence is seen.)

Conclusion

Evidently many of the surface fragments projected backwards from a broken window are of a size that allows application of the techniques described here [4]. Thus, indepen-

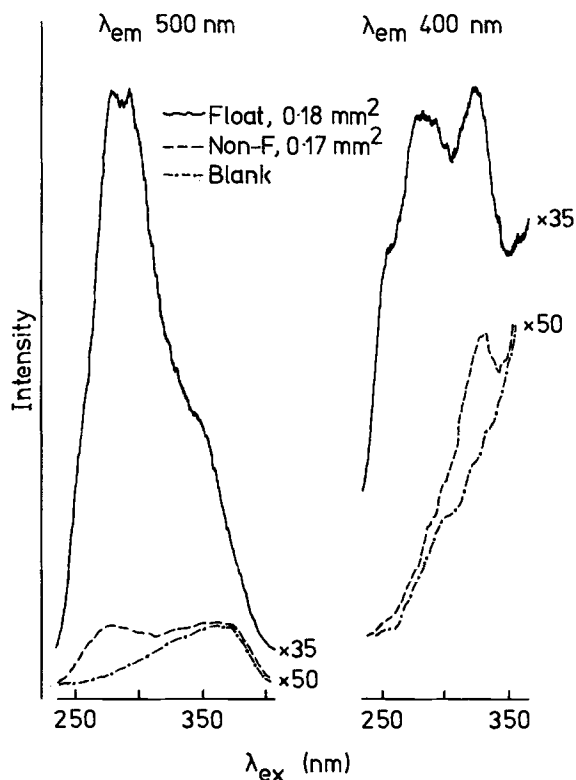


FIG. 13—Excitation spectra, monitored at 500 and 400 nm, recorded with the MPF-4, of fragments carrying the indicated surfaces from a sample of float glass. Sensitivities are marked on the spectra.

dent of the surface refractive index effect, and with less ambiguity, float and nonfloat surfaces are distinguishable over most of the size range available in case work. From larger fragments, such as from toughened glasses, further comparisons between recovered and control fragments are possible. The necessary equipment is already commonly available, and the measurements can be quickly done. There now seems to be little reason why a forensic scientist should not, in many cases, show that the type of glass surface facing the person alleged to have broken it is of the same type, or not, as any incriminating fragments.

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