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Sheet or Container?—Forensic Glass Comparisons with an Emphasis on Source Classification

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ABSTRACT: The value of source-type classification for small fragments of glass encountered in trace evidence casework is restressed. The incorporation of classification techniques into the classical refractive index/density comparison scheme is described. The techniques employed are applications of those developed by the British forensic science community over the past 5 years, targeted at differentiating the 2 most common end-use types of soda-lime-silicate glasses encountered in casework—sheet glass and container glass. The results of method verification studies on 30 window glass specimens for tempered/nontempered classification and on 140 window and container glass specimens for sheet/container classification are reported. Although some limitations were revealed with the domestic samples used, the overall success of the approach was established.

KEYWORDS: forensic science, glass, trace evidence, glass classification, sheet glass, container glass, tempered glass

The probative value of minute particles of glass adhering to a defendant's or victim's clothing has been recognized for several decades [1]. Comparison of these fragments with a questioned source is common practice in many forensic science laboratories. Generally accepted techniques include comparison of physical, optical, and more recently, chemical characteristics.

Physical characteristics include color, transparency, fluorescence, thickness, surface characteristics, and density. Optical characteristics involve determinations of refractive index and dispersion. The additional value of trace elemental analysis in the discrimination of glass specimens undifferentiable by physical and optical comparisons has been demonstrated by a variety of techniques [2–11]. Specimen size, the impact of exemplar destruction, and instrument availability must all, however, be taken into consideration.

The British forensic science community has put forth a concerted effort in developing a scheme for the general classification of minute glass particles commonly encountered in forensic science investigations. Although refractive index determinations usually suffice for the recognition of the borosilicate glasses found in motor vehicle headlamps [12], the higher refractive index ophthalmic glasses, and the alkali-barium-silicate glasses (as used in televi-

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sion tube panels) [13], a nagging problem has been encountered in the potential source classification of the ubiquitous soda-lime-silicate glasses found in sheet glass, container glass, and tableware glass [2, 6, 7, 10, 13–21] (Fig. 1). These latter three end-use types of glass often have overlapping physical and optical characteristics and are likely to be encountered in random debris [22, 23], with tableware being the most unlikely of the three. For the purpose of this paper, tableware glass will be considered to be a type of container glass.

By far the most common situation in forensic glass comparisons in the United States involves the breaking of sheet glass, as found in windows and display cases. Thus, evidential significance would be greatly enhanced if the examiner could classify minute fragments recovered from a defendant's clothing as being sheet glass, as opposed to container glass. A similar situation occurs in hit-and-run cases where the suspect vehicle's windshield or side windows are broken and glass particles are recovered from the victim's clothing. In both of these instances, classification of the recovered fragments as sheet (window) glass would not only simplify initial direct testimony, but would also enable a more meaningful assessment of the evidential value of a match between a source of sheet glass and the questioned glass fragments.

Frequency of occurrence of physical and optical characteristics of flat (sheet) glass sources has been accumulated by law enforcement laboratories. One can cite this frequency as an indicator of the likelihood of randomly encountering a particular type of glass. However, if the analyst cannot assure himself that the questioned fragments recovered from the garments of a suspect or victim originated from a sheet glass source, the application of this frequency of occurrence to those questioned fragments is somewhat tenuous [23–25]. An alibi involving contact with container glass fragments, whether it be from a specific source or from general contamination, is not so far out of the ordinary that it should be dismissed. One may then ask, What is the frequency of occurrence of this type of container glass? Could the questioned fragments be a common type of container glass as opposed to a relatively uncommon type of sheet glass? Classification as sheet glass limits the likelihood of random contamination (how frequently does one's clothing come into intimate contact with broken window glass resulting in a significant transfer of that material?) and permits the extension of frequency-of-occurrence evaluation to the questioned fragments as well as to the sheet glass standard.

Background Information

A bulk of the classification research work performed to date indicates that magnesium and iron are good semiquantitative marker elements for the discrimination of sheet glass

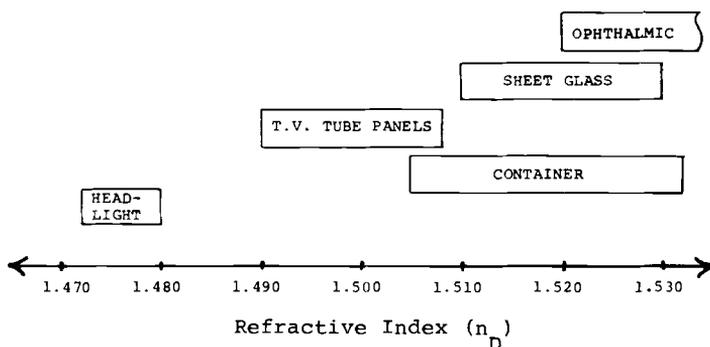


FIG. 1—General refractive index ranges of source types of glass.

versus container glass [6, 7, 10, 14-19]. It is also suggested that arsenic and barium can be utilized as additional classifying elements [10, 15-19]. Details can be found in the respective references.

Although semiquantitative determination of elemental constituents provides a reasonably reliable classification of small soda-lime-silicate glass fragments, three other techniques have also been developed which provide equally reliable classification without the need for use of elaborate instrumentation. First of all, Underhill [26] reported a technique for recognizing float glass via microscopic observation. Float glass, a particular type of sheet glass, thus has characteristics which afford a means of classification. Confirmation of a thin deposit of tin on the float surface of the minute particle can be effected by means of scanning electron microscope/X-ray fluorescence microprobe (SEM-microprobe) techniques if desired. Secondly, Locke et al.² reported a technique for the classification of minute glass particles as tempered versus nontempered. The approach involves the determination of refractive index both before and after laboratory annealing. In that tempered glass is found only in sheet glass applications (container glass did not yield "tempered" results), a fragment which classifies as tempered would also qualify as a type of sheet glass. Finally, Locke [27] has also reported the use of a microscopic interferometer to study the surface topology of minute glass fragments. Interference fringes produce patterns which permit the differentiation of sheet glass and container glass if surface fragments are present in the questioned material.

Use of the "microscopic" classification techniques provides a simpler and less expensive approach to the classification problem, although not an all-encompassing solution. The first two techniques referenced above permit a more specific classification of subgroups of sheet glass (for example, float and tempered), but are not effective for classifying sheet/nonsheet glasses which do not fall into the specific subgroups. The third method is more generally applicable for sheet/nonsheet classification, but is effective only when surface fragments are present in the recovered debris.

Analytical Approach

Concepts taken from the classification methods developed in England were incorporated into existing examination procedures. Developed techniques were essentially added to the existing physical and optical comparisons routinely employed in glass particle examinations. The additions are comprised primarily of elemental analyses for the estimation of magnesium and iron levels and an annealing process designed to detect the degree of residual stress as evidenced by the change in the refractive index brought on by annealing.

Initially, questioned and standard glass fragments are compared for physical attributes such as color, transparency, thickness (if full thickness fragments are present), and surface characteristics. The fragments are then compared for fluorescence under shortwave ultraviolet light. Float sheet glass fluoresces strongly on the surface that is exposed to the molten tin during the manufacturing process.

At this point, indistinguishable specimens are compared by optical and density characteristics. The procedure closely follows that set out by Miller [20]. The double-variation method is used for refractive index and dispersion measurements. The sink/float technique, in conjunction with vacuum transfer of the balance liquid to a Mettler DMA 46 density meter, is used for density measurements. Particular attention is paid to viewing several particles during the refractive index determination in an attempt to assess source variations as well as to detect the presence of Underhill's "tramlines" [26], which are taken to be characteristic of float sheet glass.

Corresponding fragments are subsequently recovered and washed in acetone. They are

²J. Locke, D. G. Sanger, and G. Roopnarine, "The Identification of Toughened Glass by Annealing, Home Office Central Research Establishment Report 421, 1981.

then mounted on graphite SEM stubs using a minimum of carbon-conductive paint³ to tack them onto the stub's surface. One should be careful to select the orientation such that the area to be analyzed is as close to parallel to the stub surface as possible. Variations in takeoff angles of as much as $\pm 15^\circ$ have not altered the calcium-to-magnesium (Ca/Mg) peak ratios to the point of affecting classification. The SEM stub, with adhering uncoated glass particles, is then placed into an oven to dry at approximately 70°C . It is then introduced into an AMR 1000 scanning electron microscope equipped with an EDAX PV9100/70 X-ray fluorescence spectrometer. Each particle is subjected to a 20-kV electron beam after being positioned at a 12-mm working distance with a 45° stage tilt. Data are collected until a 40 000 count preset on the calcium K_α window is satisfied. Ca/Mg ratios are determined following background subtraction and peak intensity calculation. These ratios are subsequently used for sheet/container glass classifications.

The particles are removed from the SEM stub by placing a drop of acetone on the stub surface and retrieving the fragments following acetone dissolution of the mounting paint. They are then washed and rinsed in clean acetone. The glass fragments are then tacked onto Kapton X-ray film⁴ using either carbon-conductive paint or clear nail polish.⁵ Care is taken to minimize the amount of mounting medium used so as to prevent capillary draw of the liquid past the edges of the particles when they are placed onto the droplets. Again, efforts are made to orient specimens with their flattest surface parallel to the film surface in an effort to reduce variations resulting from takeoff angle effects. The mounting medium is permitted to dry before stretching the film across an aperture, cut out of a plastic frame, and affixing it with transparent tape (Fig. 2).

The specimen assembly is placed into the chamber of an EDAX PV9500 X-ray fluorescence spectrometer in an inverted position so that the particles are in the direct path of the

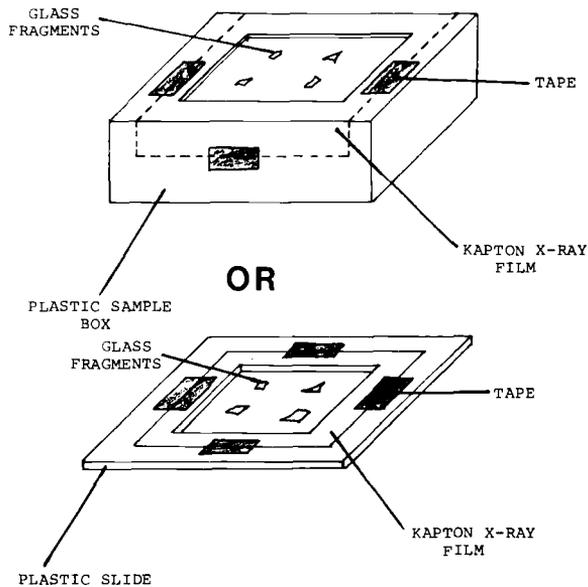


FIG. 2—X-ray fluorescence (XRF) specimen mounts.

³TV Tube Coat, Ted Pella, Inc., P.O. Box 510, Tustin, CA 92681.

⁴Kapton X-ray film, Spex Industries, Inc., 3880 Kark Ave., Metuchen, NJ 08840.

⁵Cutex Nail Polish, #07 Colorless Cream.

X-ray tube and energy-dispersive detector, which lie below the specimen plane. Initially, the specimens were manually centered in the chamber before each particle analysis; however, the subsequent installation of an automated precision *x-y* stage⁶ permits specimens to be consecutively positioned in the beam (± 0.1 mm) without visual alignment or chamber opening. The particles are subjected to an X-ray beam, in vacuo, which has been collimated to 3 mm. The beam is supplied by a rhodium target X-ray tube operated at a potential of 35 kV and a current of 500 μ A. No primary filter is used. Data are collected until a 40 000 count preset on the calcium K_{α} peak is satisfied. Background is subtracted and peak intensities are determined for all elements detected. Calcium/iron (Ca/Fe) ratios are then calculated and used for sheet/container classifications. Overall elemental profiles are used for comparison purposes, keeping in mind the limitations of the technique for small, irregularly shaped specimens [10].

Corresponding fragments are recovered from the X-ray film by acetone wetting and then washed with acetone in ultrasonic agitation. In that the next portion of the examination will result in a change in the evidence's physical and optical properties, only a portion of the particle is broken off and used. If this is not possible, the whole particle must be used. Considering evidence preservation requirements, a judicious decision concerning representative sampling may be in order at this point.

The specimens are placed into chambers in a stainless steel annealing block like that described by Locke [28]. The block, holding both questioned and standard glass fragments, is placed into a Thermolyne Model 1400 muffle furnace and subjected to an annealing routine consisting of heating to 550°C, holding for 1 h, then shutting off the power and permitting the furnace to cool slowly at its own rate. The particles are then recovered and rebroken to permit the determination of their refractive index at the sodium D line (589 nm) using the same method as employed for the initial refractive index and dispersion determinations. The change in refractive index (Δn_D) is calculated and used to classify the respective particle as tempered or nontempered. If necessary, fragments may be recovered from the silicone immersion oil and washed in acetone.

Discussion

The comparison of physical and optical attributes in the discrimination of similar glass samples has been well documented over the past 35 years. In that this work is intended to focus on the incorporation of additional methods of source classification into the analytical scheme currently used for forensic glass comparison, I will not dwell on justifications for the use of density, refractive index, and dispersion characteristics in the analytical approach. Suffice it to say that I have learned from the data of Miller [20] and have heeded the warning of Stoney and Thornton [29] concerning the failure to make the distinction between ultimate discrimination power and the usefulness of particular properties for individualization.

The location of flat surfaces on glass particles is difficult. Recognition of fragments with such surfaces provides valuable information, including potential sheet glass classification or float sheet glass classification. As noted by Zoro [30], as many as one third of the backward-flying fragments originating from a broken window have some of the original flat surface present. The present author has not yet acquired the interference objective described by Locke [27], but is convinced of its application for sheet glass recognition based on preliminary investigations. In its absence, the location of flat surfaces on surface particles is pursued by the search for the flash of reflected light and for featureless surface topology while tipping the fragment under stereoscopic observation with low-angle oblique lighting. This has proven relatively successful in properly orienting particles for shortwave ultraviolet light

⁶GTP X-Y Positional Control System, G.T.P. Engineering Co., Ltd., supplied through EDAX International, Prairie View, IL.

fluorescence examination in an effort to identify float glass surfaces. Good correlation has been found between observed fluorescence and subsequent observation of Underhill's "tramlines" [26] during refractive index determinations. Identification of surface tin deposits via SEM-microprobe examination has served to further substantiate the float glass classification. This method is one very effective way of determining that questioned glass fragments originated from a sheet glass source.

Occasionally, when larger glass fragments are encountered, stereomicroscopic examination will reveal the characteristic shape or fracture surface morphology of tempered glass. The general cube shape, along with the multiple hackle and conchoidal striae on the fracture surface (mirror-imaged on either side of a central thickness frost line), is sufficient for classification as tempered glass (Fig. 3). The forensic glass examiner encounters tempered glass in store windows, glass doors, display cases, residential sliding glass doors, and vehicle side and rear windows. All of these end-use applications are of a sheet glass nature. The tempered glass morphology is not seen in container glass. It may be encountered in ophthalmic glass; however, thickness variations are usually a good preliminary indication of this type of application. Thus, the classification of tempered glass discriminates between sheet glass and container glass.

Unfortunately, a majority of forensic glass cases are confined to questioned fragments smaller than 1 mm in length and often weighing as little as 50 to 100 μg [22,30-32]. A desire to still be able to classify these tiny fragments as tempered or nontempered prompted the evaluation of the method proposed by Locke et al.² This method contrasts residual stress in tempered versus nontempered particles by monitoring refractive index both before and after laboratory annealing. As mentioned in the Analytical Approach section, the technique does alter the optical and physical properties of the evidence particle; however, its potential for small specimen size requirements permits splitting of the specimen for preservation of evidence. If the specimen size is too small for splitting and the decision to alter the evidence is considered to be the best approach, the technique can be performed following all other non-destructive examinations described and still maintain at least the general form of the original evidential material.

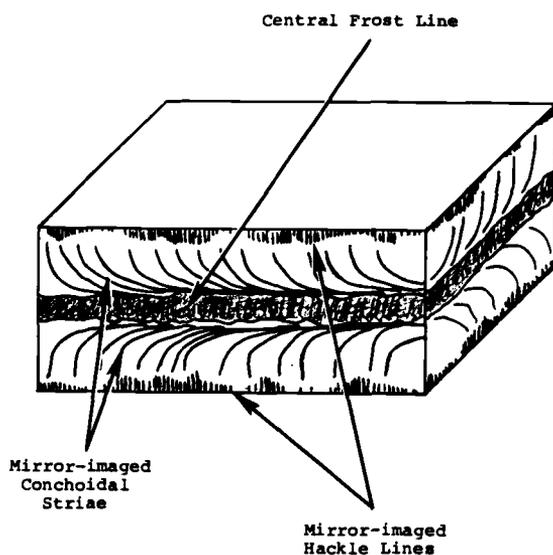


FIG. 3—Tempered glass fragment morphology.

Initial evaluation of the technique was performed using the original methodology reported by Locke et al.² This technique used small crucibles and an overnight hold of the furnace temperature at the annealing point, as contrasted to the present method [28] utilizing a stainless steel annealing block with only a 1-h hold at the annealing point. Approximately 30 specimens of architectural and motor vehicle window glasses were tested, including tempered and nontempered float, tempered and nontempered nonfloat, and laminated vehicle windshield. The results can be seen in Fig. 4. As reported by Locke et al.,² a marked discrimination between tempered and nontempered glass was observed. However, the observed demarcation of the change in refractive index (Δn_D) in this study was at 125×10^{-5} as opposed to that of Locke, which fell at 150×10^{-5} (Fig. 5). This is probably due to differences in the furnaces, as evidenced by oven cooldown in 3 h rather than 5 h. As noted by Locke, the slower the oven cooldown, the greater the Δn_D .

Locke's work also demonstrated excellent classification for "toughened windscreens."² Vehicles in the United States use partially tempered laminated glass as windshields, with tempered glass used in side and rear windows [20,33]. This manufacturing thermal history is apparent in the Δn_D observed in the eight windshield glasses tested. Referring to Fig. 4, it can be seen that this type of glass defies the classification scheme. This is not surprising when one remembers that these glasses are manufactured with varying degrees of tempering.

Consequently, the method proposed by Locke et al.² seems to work very nicely. Glass spec-

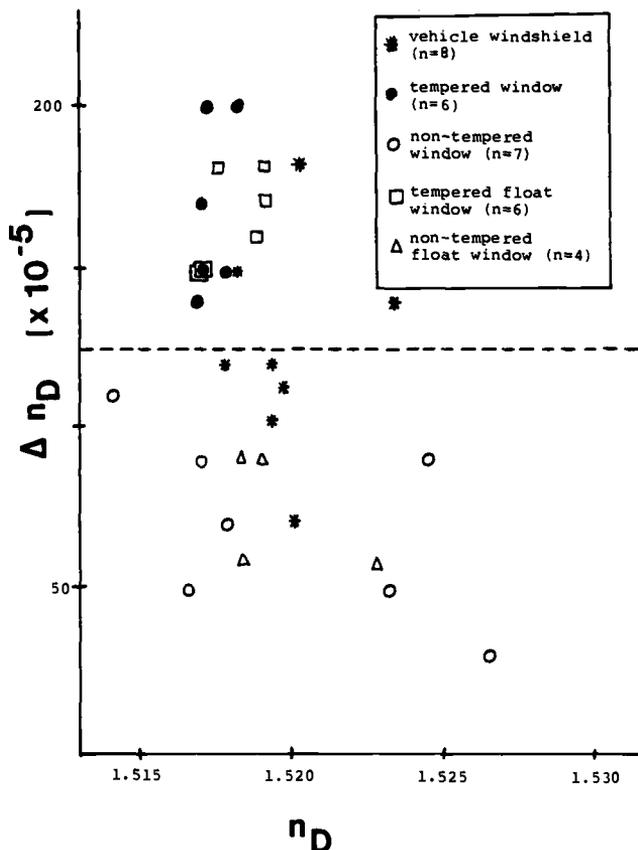


FIG. 4—Change in refractive index with laboratory annealing of class types of glass—domestic study.

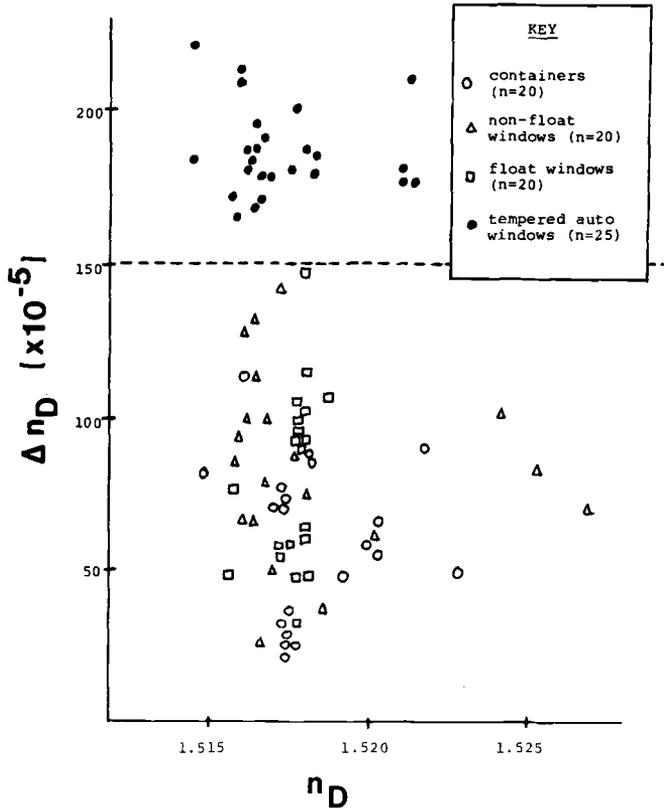


FIG. 5—Change in refractive index with laboratory annealing of class types of glass—HOCRE study.²

imens exhibiting a Δn_D above the demarcation line can be classified as having originated from a tempered sheet glass, while glasses exhibiting a Δn_D below the demarcation line can be classified as having originated from a nontempered origin or a partially tempered laminated vehicle windshield. Thus, another specific type of sheet glass can be recognized on the particle level—tempered glass.

Following Locke's published refinement of the annealing method [28], further tests were performed to verify the use of his annealing block with short annealing point holds. The method was adopted, as described in the Analytical Approach section, following results indicating improved precision (Δn_D variance on the order of 1×10^{-4}). The reduced run time had only a slight effect on the Δn_D demarcation threshold for tempered/nontempered classification, reducing it from 12.5×10^{-4} to 11.5×10^{-4} .

In a further attempt to achieve source classification on a routine basis, work was initiated to verify sheet/container classification based on semiquantitative analysis of magnesium and iron in small glass particles. The ultimate desire to maintain evidence integrity via nondestructive instrumental techniques led to the use of X-ray fluorescence spectroscopy. The approach was patterned after the work done by Howden et al. [10], and Keeley and Christofides [16].

The SEM-microprobe is suited particularly well for nondestructive small specimen elemental analysis. Unfortunately, it suffers lower limit of detection constraints such that only

the major elements in soda-lime-silicate glasses can be detected. The magnesium levels, normally around 1 to 2% [2, 15, 16], are easily detected while the iron levels, normally around 0.01 to 0.2% [2, 15, 16], quite often escape the detection threshold of approximately 0.1%. To offset this problem, Keeley and Christofides proposed using the SEM-microprobe for magnesium level determination and a small sample X-ray fluorescence spectrometer (XRF) for iron level determination [16]. The two techniques are complementary. First of all, both are nondestructive. Secondly, while the instrument using particle excitation (SEM-microprobe) provides poor sensitivity for higher atomic weight elements, it does offer improved sensitivity for the lower atomic weight elements. In contrast, the instrument using photon excitation (XRF spectrometer) is not limited by Bremsstrahlung and offers much greater sensitivity for higher atomic weight elements. This technique, however, suffers detection constraints for the lower atomic weight elements as a result of penetration, excitation efficiency, and scatter effects. Thus, where the one is weak the other is strong.

SEM-microprobe is run as an initial elemental screening technique. Specimen preparation is quite simple and was chosen for speed, not optical quality. The technique was found to work quite well within the constraints of the proposed classification scheme. To determine their calcium-to-magnesium ratios 140 glass specimens were analyzed. They consisted of 65 sheet glass specimens, 65 bottle/jar glass specimens, and 10 tableware specimens. The sheet glass specimens included float, nonfloat, tempered, nontempered, plate, tinted plate, and laminated types over a wide range of refractive indices ($n_D = 1.5130$ to 1.5270). No attempt was made to correlate the Ca/Mg ratio to refractive index.

Initial investigations into the literature revealed that magnesium levels in sheet glass are normally 2% or greater, while those in colorless container glass are normally 1% or less [2, 14, 15, 17]. Later publications seem to substantiate this information [18, 19]. To get some idea of how well suited this technique is for discriminating these levels of magnesium, two Standard Reference Materials (SRM) from the National Bureau of Standards were chosen. They include SRM 1831, a sheet glass specimen with a magnesium level of 3.5%, and SRM 621, a container glass specimen with a magnesium level of 0.27%.⁷ Their spectra can be seen

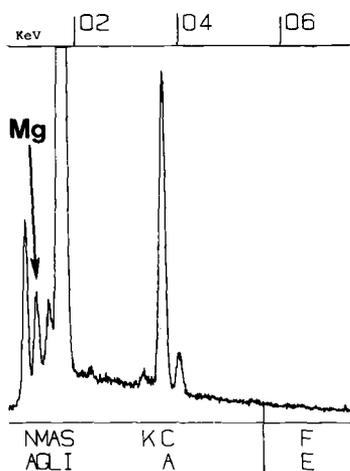


FIG. 6a—SEM microprobe X-ray fluorescence spectrum of SRM 1831 sheet glass.

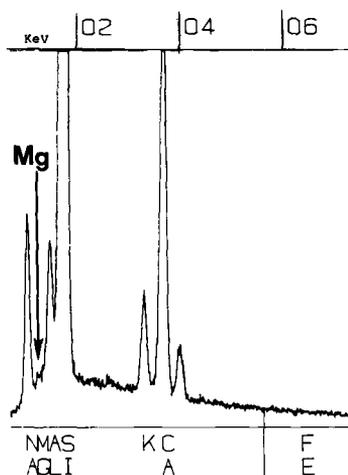


FIG. 6b—SEM microprobe X-ray fluorescence spectrum of SRM 621 container glass.

⁷Standard Reference Materials, National Bureau of Standards, U.S. Department of Commerce, Washington, DC.

in Figs. 6a and 6b. As one can see, the magnesium K_{α} peak (1.253 keV) in the sheet glass can be readily seen, whereas it is barely detectable in the container glass. The detection limit in this matrix is just about optimum for the levels encountered in the glass specimens. The Ca/Mg ratios are 5.6 and 140.6, respectively.

In running the 140 specimens, it was quickly seen that a similar trend was developing. A majority of the container glasses had barely detectable magnesium levels (Fig. 7). Several were seen to overlap into the medium to elevated levels of the sheet glasses (Fig. 8). The magnesium peak area was ratioed to the calcium peak area in an effort to reduce peak intensity variations as a result of slight differences in takeoff angles and beam current conditions. Peak areas were expressed as counts per second so as to normalize live time differences. The upper limit of the sheet glass Ca/Mg ratios was 13. Using 15 as the demarcation threshold between sheet and container Ca/Mg ratios, 61 container glasses (55 bottle/jar and 6 tableware) fell into the upper category and 79 glasses (65 sheet, 10 bottle/jar, and 4 tableware) fell into the lower category (Fig. 9). As can be seen, the split correctly classifies 81% of the container glass specimens into the upper category and misclassifies 19% of the container glass specimens into the lower category. Obviously, owing to the method of selection of the demarcation threshold, 100% of the sheet glass specimens are correctly placed into the lower category.

As was suggested by Keeley and Christofides [16], the determination of the calcium to iron ratio in the lower category specimens should rectify the misclassification of the 16 container glass specimens. The literature indicates that the iron level is approximately 0.05% or greater in sheet glass and 0.04% or lower in container glass [2, 15, 17-19]. In that these levels are below the detection limit of the SEM-microprobe, the XRF spectrometer was the instrument of choice, offering the required sensitivity without specimen destruction. Again, SRM 1831 (sheet) and 621 (container) were employed to evaluate the technique. Fragments of each measuring 300 μg were analyzed using the technique described in the Analytical Approach section. SRM 1831 has a reported iron level of 0.09%, while SRM 621 has a 0.04% iron level. Their spectra can be seen in Figs. 10a and 10b. Note the easily discernable iron K_{α} peaks (6.398 keV) as contrasted to the missing iron peaks in Figs. 6a and 6b.

In an effort to reduce the effects of variations in surface geometry and specimen size, the iron K_{α} peak intensity is ratioed to the calcium K_{α} peak (3.690 keV) intensity, as was done by

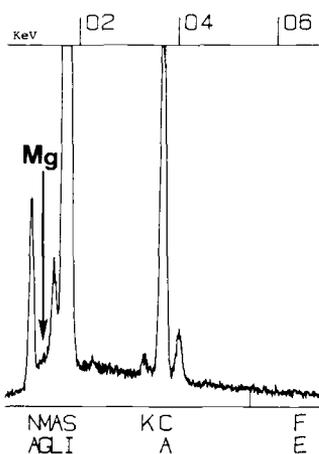


FIG. 7—SEM microprobe X-ray fluorescence spectrum of container glass with low magnesium level.

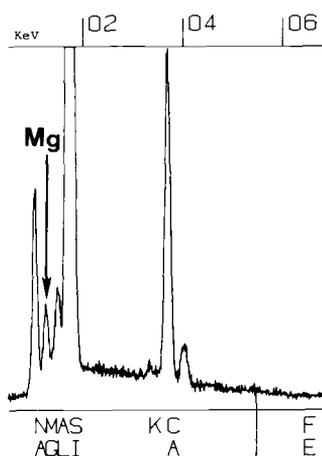


FIG. 8—SEM microprobe X-ray fluorescence spectrum of container glass with elevated magnesium level.

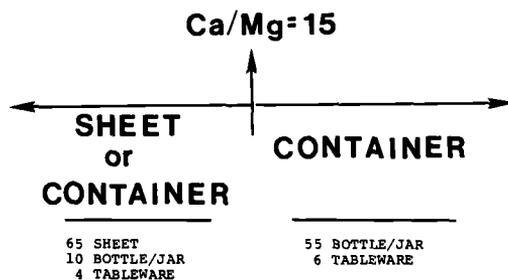


FIG. 9—Sheet/container glass classification based on SEM microprobe determination of Ca/Mg intensity ratio.

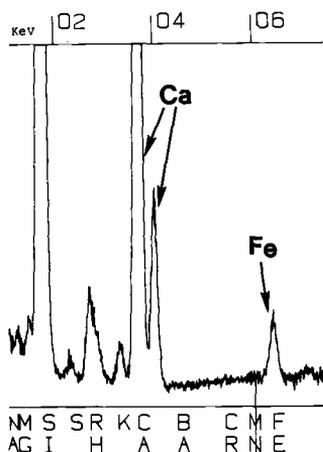


FIG. 10a—XRF spectrum of SRM 1831 sheet glass.

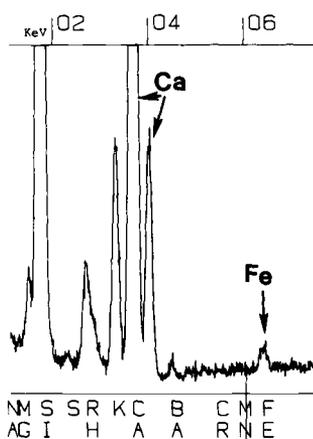


FIG. 10b—XRF spectrum of SRM 621 container glass.

Keeley and Christofides [16]. Although this reduces these variations to a satisfactory extent when comparing large differences, care must still be exercised when considering direct comparisons of very small particles. As demonstrated by Howden et al. [10], and Montecalvo [34], scattering and absorption of X-rays caused by irregular specimen shapes cause considerable variation in replicate runs. Large differences in specimen thickness produce further imprecision in intensity ratios. Because of critical depth effects, these variations are even more pronounced the greater the difference in the elements' atomic weights [10]. The Ca/Fe ratios for SRM 1831 and SRM 621 are 20 and 48, respectively. Rotating specimens produce ratio standard deviations ($2\sigma_{n-1}$) on the order of 6 to 12% (Table 1), while variation in fragment size from 2 mg down to 180 μg produces a series ratio standard deviation ($2\sigma_{n-1}$) on the order of 10% (Table 2). Although this is not severe with respect to classification efforts, some attempt should be made to subject similar size and shaped specimens to XRF analysis.

A review of the SEM-microprobe spectra revealed that none of the container glass specimens had a detectable iron K_{α} peak (6.398 keV). Of the 65 sheet glass specimens, 23 did have a pronounced iron K_{α} peak, as in Fig. 11. This size peak corresponds to a measured XRF Ca/Fe ratio of approximately 4, which is indicative of a significantly elevated iron level. Thus, an elevated magnesium level accompanied by a detectable iron level in SEM-micro-

TABLE 1—XRF Ca/Fe intensity ratio precision for varying specimen orientation.

Specimen	\bar{X}^a	$2\sigma_{n-1}^b$	$2\sigma_{n-1}, \%$
B34	40.21	4.66	11.60
B39	26.94	3.04	11.30
B44	24.58	1.50	6.10
B50	25.89	2.90	11.20
W4	27.54	2.73	9.91
W26	27.66	2.59	9.36
W48	29.79	3.52	11.82

^aMean of four determinations of the Ca/Fe ratio, rotating the specimen 90° after each analysis.

^b $2\sigma_{n-1} = 2$ (specimen standard deviation)

$$= 2 \left[\sqrt{\frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n - 1}} \right]$$

TABLE 2—XRF Ca/Fe intensity ratio precision for varying specimen size and specimen orientation on container glass B18.

Specimen Size, mg	\bar{X}^a	$2\sigma_{n-1}$	$2\sigma_{n-1}, \%$
2.034	37.63	4.38	11.64
0.741	35.53	2.64	7.44
0.583	39.39	5.41	13.73
0.334	38.56	2.48	6.43
0.365	40.06	3.89	9.71
0.188	35.89	4.91	13.68
Series	37.84	3.69	9.75

^aMean of four determinations of the Ca/Fe ratio, rotating the specimen 90° after each analysis.

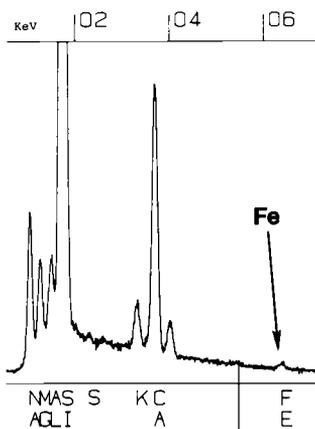


FIG. 11—Elevated iron level on SEM microprobe X-ray fluorescence spectrum of sheet glass.

probe analysis classifies the glass particle as having originated from a sheet glass origin. Consequently, only the remaining 42 sheet glass specimens and the 14 misclassified container glass specimens (Fig. 9) were subjected to XRF analysis for determination of their Ca/Fe ratios. This managed to segregate 9 of the 14 misclassified container glasses into a low iron level category (that is, high Ca/Fe ratio) and 37 of the sheet glasses into the high iron level category (that is, low Ca/Fe ratio), with 5 sheet glasses and 5 container glasses falling into an overlapping category (Fig. 12). It is suggested that multiple determinations with varying orientations be performed when Ca/Fe ratios fall within the 21 to 33 range, using the mean value as the classifying ratio. This serves to avoid classification errors caused by imprecision due to varying specimen size and shape.

A list of the glass specimens falling into the overlapping category can be found in Table 3. As can be seen, there is no correlation between source type and refractive index. Although three of the five sheet glasses have refractive indices above 1.520 (and thus fall into the upper envelope of the bimodal frequency distribution of sheet glasses received by the Federal Bu-

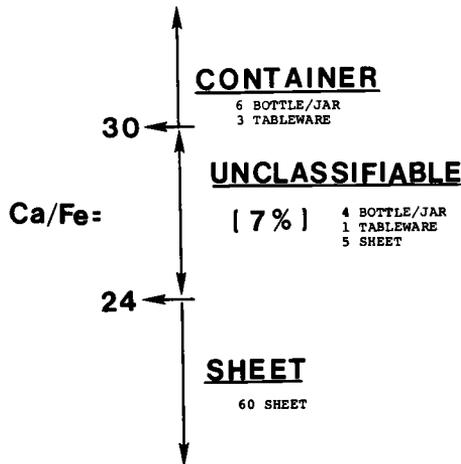


FIG. 12—Sheet/container glass classification of SEM-microprobe overlapping specimens based on XRF determination of Ca/Fe intensity ratio.

TABLE 3—Refractive indices of unclassifiable glass specimens.

Specimen	Source	$n_D^{20^\circ C}$
W4	nontempered plate glass from store window	1.5245
W9	surface texturized window from public restroom	1.5209
W26	nontempered float plate glass from store window	1.5224
W48	nontempered plate glass from residential sliding glass door	1.5169
W52	nontempered store window	1.5159
B39	Dr. Pepper returnable soda bottle	1.5136
B44	Norwich aspirin bottle	1.5139
B50	Kraft walnut topping jar	1.5167
B61	Prego spaghetti sauce jar	1.5173
T7	Tableware tumbler	1.5141

reau of Investigation laboratory [20]), two of them have refractive indices below 1.520 and obviously overlap the refractive indices of the container glass specimens. Further attempts to classify the overlapping specimens using arsenic and barium levels proved fruitless, in that the five window specimens have elemental ratios spanning the full range of the container glass elemental ratios.

Although complete classification could not be accomplished using the adapted scheme of Keeley and Christofides [16], it still provides a wealth of classification information. Using the rapid SEM-microprobe method alone, 81% of the container glasses were recognized by their low magnesium levels. Resorting to the XRF method provides proper classification of 93% of the 140 specimens examined, with 7% of them falling into an unclassifiable overlap area which can be recognized by its Ca/Fe ratio upper and lower limits (Fig. 12).

Considering that the X-ray fluorescence techniques employed required the use of elemental intensity ratios to counteract the variations produced by specimen geometry and size, the possibility of further segregation of class types by semi-quantitative determination of elemental concentrations was investigated. Although inductively coupled plasma emission spectroscopy (ICP) seems to offer the most versatile approach to the problem [11, 17, 19], DC arc emission spectroscopy was used to analyze the unclassifiable specimens because of the lack of access to ICP instrumentation [24]. Investigations indicate that all but two of the container glasses were properly classified using the iron line intensities at 259.8 and 272.1 nm. It should therefore be noted that a semiquantitative determination of elemental concentrations may provide further discrimination between sheet and container glasses at the price of increased analytical time and specimen destruction.

Conclusion

The value of source type classification for small fragments of glass evidence is founded in its ability to simplify direct court testimony and to provide a sound basis for the use of sheet glass frequency of occurrence data in evaluating the evidential significance of a match between small questioned glass fragments and a source of broken sheet glass.

Classification of source type can require techniques as simple as microscopy or as complicated as multiple types of instrumental analysis. Verification of analytical approaches developed by the British forensic science community supports the use of these techniques on domestic samples. Although many avenues of elemental analysis are available, the forensic glass examiner must always weigh the consequences of exemplar destruction. For this reason, X-ray fluorescence techniques have a substantial advantage.

It is hoped that the work presented in this report will spark further investigations on domestic samples and provide an increased awareness of the value of this extended analytical approach.

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References

- [1] Kirk, P. L., *Density and Refractive Index—Their Application in Criminal Identification*, Charles C Thomas, Springfield, IL, 1951, pp. 1-80.
- [2] Dabbs, M. D., German, B., Pearson, E. F., and Scaplehorn, A. W., "The Use of Spark Source Mass Spectrometry for the Analysis of Glass Fragments Encountered in Forensic Applications, Part 2," *Journal of the Forensic Science Society*, Vol. 13, 1973, pp. 281-286.

- [3] Coleman, R. F. and Goode, G. C., "Comparison of Glass Fragments by Neutron Activation Analysis," *Journal of Radioanalytical Chemistry*, Vol. 15, 1973, pp. 367-388.
- [4] Butterworth, A., German, B., Morgans, D., and Scaplehorn, A., "A Report on an Investigation into the Trace Elements Present in Vehicle Headlamp and Auxiliary Lamp Glasses," *Journal of the Forensic Science Society*, Vol. 14, No. 1, 1974, pp. 41-45.
- [5] Andrasko, J. and Maehly, A. C., "The Discrimination Between Samples of Window Glass by Combining Physical and Chemical Techniques," *Journal of Forensic Sciences*, Vol. 22, No. 1, Jan. 1977, pp. 250-262.
- [6] Hughes, J. C., Catterick, T., and Southard, G., "The Quantitative Analysis of Glass by Atomic Absorption Spectroscopy," *Forensic Science*, Vol. 8, 1976, pp. 217-227.
- [7] Blacklock, E. C., Rogers, A., Wall, C., and Wheals, B. B., "The Quantitative Analysis of Glass by Emission Spectrography: A Six Element Survey," *Forensic Science*, Vol. 7, 1976, pp. 126-130.
- [8] Reeve, V., Mathiesen, J., and Fong, W., "Elemental Analysis by Energy Dispersive X-ray: A Significant Factor in the Forensic Analysis of Glass," *Journal of Forensic Sciences*, Vol. 21, No. 2, April 1976, pp. 291-306.
- [9] Haney, M. A., "Comparison of Window Glasses by Isotope Dilution Spark Source Mass Spectrometry," *Journal of Forensic Sciences*, Vol. 22, No. 3, July 1977, pp. 534-544.
- [10] Howden, C. R., Dudley, R. J., and Smalldon, K. W., "The Analysis of Small Glass Fragments Using Energy Dispersive X-ray Fluorescence Spectrometry," *Journal of the Forensic Science Society*, Vol. 18, 1978, pp. 99-112.
- [11] Hickman, D. A., "Elemental Analysis and the Discrimination of Sheet Glass Samples," *Forensic Science International*, Vol. 23, 1983, pp. 213-223.
- [12] *Law Enforcement Standards Program, Report 0605.00, The Characterization of Auto Headlight Glass by Refractive Index and Density*, U.S. Government Printing Office, Washington, DC, 1976.
- [13] MacDonell, H. L., "Identification of Glass Fragments," *Journal of Forensic Sciences*, Vol. 9, No. 2, April 1964, pp. 244-254.
- [14] Howden, C. R., German, B., and Smalldon, K. W., "The Determination of Iron and Magnesium in Small Glass Fragments Using Flameless Atomic Absorption Spectrophotometry," *Journal of the Forensic Science Society*, Vol. 17, No. 1, Jan. 1977, pp. 153-159.
- [15] German, B., Morgans, D., Butterworth, A., and Scaplehorn, A., "A Survey of British Container Glass Using Spark Source Mass Spectrometry With Electrical Detection," *Journal of the Forensic Science Society*, Vol. 18, 1978, pp. 113-121.
- [16] Keeley, R. H. and Christofides, S., "Classification of Small Glass Fragments by X-ray Microanalysis with the SEM and a Small Sample XRF Spectrometer" in *Proceedings of Scanning Electron Microscopy*, SEM Inc., AMF, O'Hare, IL, 1979, pp. 459-464.
- [17] Hickman, D. A., "A Classification Scheme for Glass," *Forensic Science International*, Vol. 17, 1981, pp. 265-281.
- [18] Hickman, D. A., Harbottle, G., and Sayre, E. V., "The Selection of the Best Elemental Variables for the Classification of Glass Samples," *Forensic Science International*, Vol. 23, 1983, pp. 189-212.
- [19] Hickman, D. A., "Linking the Criminals to the Scene of the Crime with Glass Analysis," *Analytical Chemistry*, Vol. 56, No. 7, 1984, pp. 844A-852A.
- [20] Miller, E. T., "Forensic Glass Comparisons," in *Forensic Science Handbook*, R. Saferstein, Ed., Prentice-Hall, Englewood Cliffs, NJ, 1982, pp. 139-183.
- [21] Lambert, J. A. and Evett, I. W., "The Refractive Index Distribution of Control Glass Samples Examined by the Forensic Science Laboratories in the United Kingdom," *Forensic Science International*, Vol. 26, 1984, pp. 1-23.
- [22] Pearson, E. F., May, R. W., and Dabbs, M. D. G., "Glass and Paint Fragments Found in Men's Outer Clothing—Report of a Survey," *Journal of Forensic Sciences*, Vol. 16, No. 3, July 1971, pp. 283-300.
- [23] Harrison, P. H., Lambert, J. A., and Zoro, J. A., "A Survey of Glass Fragments Recovered From Clothing of Persons Suspected of Involvement in Crime," *Forensic Science International*, Vol. 27, 1985, pp. 171-187.
- [24] Ryland, S. G., "A Prospective Method for the Differentiation of Window and Container Glass Fragments," Southern Association of Forensic Scientists 1981 Fall Seminar, Birmingham, AL, 1981.
- [25] Stoney, D. A., "Evaluation of Associative Evidence: Choosing the Relevant Question," *Journal of the Forensic Science Society*, Vol. 24, No. 5, 1984, pp. 473-482.
- [26] Underhill, M., "Multiple Refractive Index in Float Glass," *Journal of the Forensic Science Society*, Vol. 20, 1980, pp. 169-176.
- [27] Locke, J., "New Developments in the Forensic Examination of Glass," *The Microscope*, Vol. 32, No. 1, 1984, pp. 1-32.
- [28] Locke, J., Hayes, C. A., and Sanger, D. G., "The Design of Equipment and Thermal Routines for Annealing Glass Particles," *Forensic Science International*, Vol. 26, 1984, pp. 139-146.

- [29] Stoney, D. A. and Thornton, J. I., "The Correlation of Density and Refractive Index in Glass—Forensic Considerations," *California Association of Criminalists Newsletter*, Fall 1979, pp. 3-12.
- [30] Zoro, J. A., "Observations on the Backward Fragmentation of Float Glass," *Forensic Science International*, Vol. 22, 1983, pp. 213-219.
- [31] Pounds, C. A. and Smalldon, K. W., "The Distribution of Glass Fragments in Front of a Broken Window and the Transfer of Fragments to Individuals Standing Nearby," *Journal of the Forensic Science Society*, Vol. 18, 1978, pp. 197-203.
- [32] Brewster, F., Thorpe, J., Gettinby, G., and Caddy, B., "The Retention of Glass Particles on Woven Fabrics," *Journal of Forensic Sciences*, Vol. 30, No. 3, 1985, pp. 798-805.
- [33] *Glass, The Encyclopedia of How It's Made*, D. Clarke, Ed., A&W Publishers, New York, 1978, pp. 73-79.
- [34] Montecalvo, F., "Problems Encountered in X-ray Fluorescence Analysis of Small Glass Particles," *Crime Lab Digest*, Vol. 77, No. 9, Dec. 1977, pp. 4-9.

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