

Scott Ryland, B.S.¹

Discrimination of Flat (Sheet) Glass Specimens Having Similar Refractive Indices Using Micro X-Ray Fluorescence Spectrometry

ABSTRACT: It has been reported that discrimination between sources of broken flat (sheet) glass can be substantially improved when trace element profiles are compared in addition to refractive index alone. This paper reports on the discrimination power afforded by micro X-ray fluorescence spectrometry on two sets of randomly encountered sources of broken flat glass having nominal refractive indices of 1.5184 to 1.5185 (37 samples) and 1.5180 to 1.5182 (30 samples) at 20.0 degrees C. The results indicate discrimination powers on the order of 98.0 to 99.5 percent for both trial sets using either a conservative ± 3 standard deviations criterion or a T-test criterion at 95 percent confidence level.

KEYWORDS: Forensic, glass comparisons, discrimination study, X-ray fluorescence spectrometry

Small fragments of broken flat window glass are occasionally encountered in forensic investigations involving homicide, home invasion, motor vehicle hit and run, and property crime. Typically, it is requested that fragments recovered at the scene or on the clothing of a suspect (questioned sample) be compared to the glass from a broken window of known origin (known sample) in an effort to determine if they are alike. One of the most common analytical techniques used for discrimination between samples is the precise determination of their refractive indices (1, 2). If the samples are found to be different it is concluded that the two could not have had a common origin. If they are found to be indistinguishable it is concluded that the questioned glass could have originated from the known broken window. In the author's experience, this characteristic alone is quite discriminating and often differentiates from ninety to ninety-eight percent of randomly selected samples of flat glass. However, it has been reported that discrimination between sources of broken flat (sheet) glass can be substantially improved when trace elements are compared in addition to refractive index alone (1, 2, 3, 4). One method for comparison of trace elements in small fragments of

¹ Florida Department of Law Enforcement, Orlando Regional Operations Center, 500 W. Robinson St., Orlando, FL, USA, 32801.

Table 1: Sample Set 1 (nD=1.5184–1.5185)

Sample Number	Year Entered	nD at 20° C.	Float	Tempered	End Use
W23	1980	1.5184	Yes	Yes	vehicle side window
W33	1980	1.5185	Yes	Yes	vehicle side window
W49	1982	1.5185	Yes	No	store window
W62	1984	1.5184	Yes	No	store window
W79	1986	1.5185	Yes	No	store plate glass
W83	1987	1.5184	Yes	Yes	vehicle side window
W95	1989	1.5185	Yes	Yes	vehicle side window
W103	1987	1.5184	Yes	Yes	vehicle side window
W107	1990	1.5185	Yes	Yes	vehicle side window
W129	1995	1.5185	No	Yes	sliding glass door
W132	1993	1.5185	Yes	No	display case
W142	1995	1.5185	Yes	No	laminated store window
W143	1995	1.5185	Yes	No	laminated store window
W152	1995	1.5185	Yes	No	bathroom window (outer)
W153	1995	1.5185	No	No	bathroom window (inner)
W165	1996	1.5184	Yes	Yes	store window
W174	1996	1.5184	Yes	Yes	vehicle side window
W193	1996	1.5185	Yes	Yes	vehicle rear window
W204	1997	1.5185	Yes	No	store window
W206	1997	1.5185	Yes	No	store window
W232	1997	1.5185	Yes	No	business window
W248	1998	1.5184	Yes	Yes	residence window
W255	1999	1.5185	Yes	Yes	business window
W259	1999	1.5184	Yes	Yes	business window
W266	2000	1.5185	Yes	No	business window
W285	2000	1.5185	Yes	Yes	business window
W319	2002	1.5185	Yes	No	laminated store window
W320	2002	1.5185	Yes	No	laminated store window
W323	2002	1.5185	Yes	Yes	vehicle side window
W340	2002	1.5185	Yes	Yes	vehicle side window
W350	2003	1.5184	Yes	Yes	vehicle side window
W351	2003	1.5184	Yes	Yes	vehicle rear window
W352	2002	1.5185	No	No	business window
W360	2002	1.5184	Yes	No	laminated store window
W368	2003	1.5184	Yes	No	residence window
W383	2004	1.5184	Yes	No	residence window
W399	2004	1.5184	No	Yes	business door

broken glass is micro X-ray fluorescence spectrometry (μ -XRF). It is not only sensitive to the major elements present in soda-lime-silicate glass but also to the minor and trace elements present, with detection limits on the order of tens of parts-per-million (ppm) for elements such as Ti, Mn, As, Rb, Sr, and Zr (5). Furthermore, its totally non-destructive nature permits it to be used at any point during the analytical scheme. Improved discrimination using μ -XRF has been previously reported in the literature (6, 7, 8), but often not with larger sets of samples known to have similar refractive indices.

This project evaluates the discrimination power of μ -XRF on two sets of randomly encountered sources of broken flat glass having nominal refractive indices of 1.5184 to 1.5185 (37 samples and designated Set 1) and 1.5180 to 1.5182 (30 samples and designated Set 2) at 20.0 degrees C. The samples were selected from a reference collection of sheet glass samples comprised of standards submitted in cases received from agencies throughout the state of Florida, USA, from 1979 to 2005 (Tables 1 and 2). Considering the sampling method, it is reasonable to assume that the samples in the reference collection are random and to some extent represent the population of broken flat glass in the state of Florida. Refractive index distributions in the glass collection of over five hundred samples indicate similar patterns between older architectural glass (received in casework from 1979 to 1997) and newer architectural glass (received in casework from 1998 to 2010). That is not the case for vehicle glass however. This observation is not at all surprising considering the difference in service life for architectural glass versus vehicle glass.

Individual panes of laminated architectural and vehicle windows were treated as separate samples since they are sometimes discriminated by either their refractive indices or elemental compositions.

Table 2: Sample Set 2 (nD=1.5180-1.5182)

Sample Number	Year Entered	nD at 20° C.	Float	Tempered	End Use
W2	1979	1.5181	No	No	unknown
W5	1979	1.5181	No	No	residence window
W37	1980	1.5181	Yes	No	unknown
W47	1982	1.5180	Yes	No	fire extinguisher case
W98	1989	1.5180	Yes	Yes	vehicle side window
W100	1989	1.5182	Yes	No	vehicle windshield (outer)
W106	1990	1.5181	Yes	Yes	store window
W144	1995	1.5181	Yes	Yes	vehicle side window (rear)
W145	1995	1.5181	Yes	Yes	vehicle side window (front)
W149	1995	1.5180	No	Yes	business window
W178	1996	1.5180	Yes	No	residence window
W189	1996	1.5182	Yes	Yes	business window
W210	1997	1.5180	Yes	Yes	business window
W213	1997	1.5181	Yes	Yes	vehicle side window
W219	1997	1.5180	No	Yes	store window
W222	1998	1.5182	Yes	No	store window
W224	1997	1.5180	Yes	Yes	vehicle side window
W234	1997	1.5180	Yes	Yes	business window
W235	1997	1.5180	Yes	No	business window
W241	1998	1.5182	Yes	Yes	business door
W245	1998	1.5181	Yes	Yes	vehicle sunroof
W252	1999	1.5182	Yes	No	residence window
W264	1998	1.5182	No	No	vehicle side view mirror
W272	2000	1.5180	Yes	Yes	vehicle side window
W282	2001	1.5182	Yes	Yes	vehicle side window
W293	2001	1.5181	Yes	No	business window
W295	2001	1.5181	Yes	Yes	business window
W346	2002	1.5182	Yes	Yes	vehicle side window
W393	2004	1.5181	Yes	No	business door
W394	2004	1.5181	Yes	No	business door

Samples for the two trial sets were chosen from high frequency refractive index populations without regard to age, heat strengthened type (tempered versus annealed), or end use application (architectural versus automotive). Obviously, once samples were selected based on their particular refractive index range the sample sets were no longer random. This is evidenced by the paucity of windshield glass in both sets. A majority of the samples are from architectural sources and there is a reasonably even distribution of tempered

versus non-tempered glass in the trial sets. The refractive index values recorded for the reference collection are mean values reported to only four decimal places and corrected to 20.0 degrees C. Hence, they are nominal values and do not guarantee that some of the samples within each set could be discriminated by detailed side by side comparison using a sensitive method such as Foster + Freeman’s GRIM².

METHODS OF ANALYSIS

The refractive indices of the first twenty-one of the thirty-seven samples of Set 1 were inter-compared using a Foster + Freeman GRIM in order to evaluate the discrimination power provided by pair-wise comparison of the nominally similar refractive indices using a sensitive method. This initial set was analyzed as part of a

² Foster + Freeman, Ltd., Vale Park, Evesham, Worcestershire, WR11 1TD, UK.

previous exercise designed to compare the discrimination power of micro X-ray fluorescence spectrometry, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and laser induced breakdown spectrometry (LIBS) (7). Mean refractive indices, ranges, and standard deviations were determined for each of the twenty-one samples at one wavelength.

Following that, the full sets of thirty-seven samples and thirty samples having nominally similar refractive indices were analyzed by μ -XRF. They were inter-compared on a pair-wise basis using spectral overlay evaluation and comparison of selected element intensity ratios using a ± 3 standard deviation criterion and a T-test criterion. Although the former intensity ratio criterion is what the author uses in routine casework, the latter was chosen to be more consistent with the criterion used in current publications evaluating LA-ICP-MS. Spectral overlay comparisons permitted detection of different elements and grossly differing element peak intensities (Figure 1). Peak intensity ratio comparisons permitted more precise comparisons of semi-quantitative characteristics and also served to minimize the effects of inherent take-off angle variations between replicate samples (Figures 2 and 3).

Figure 1: Samples W340 and W352 from Set 1 demonstrate clear differences in As and K content. The spectra are normalized to the most intense peak (Si K α) and displayed with an expanded intensity scale to visualize trace components.

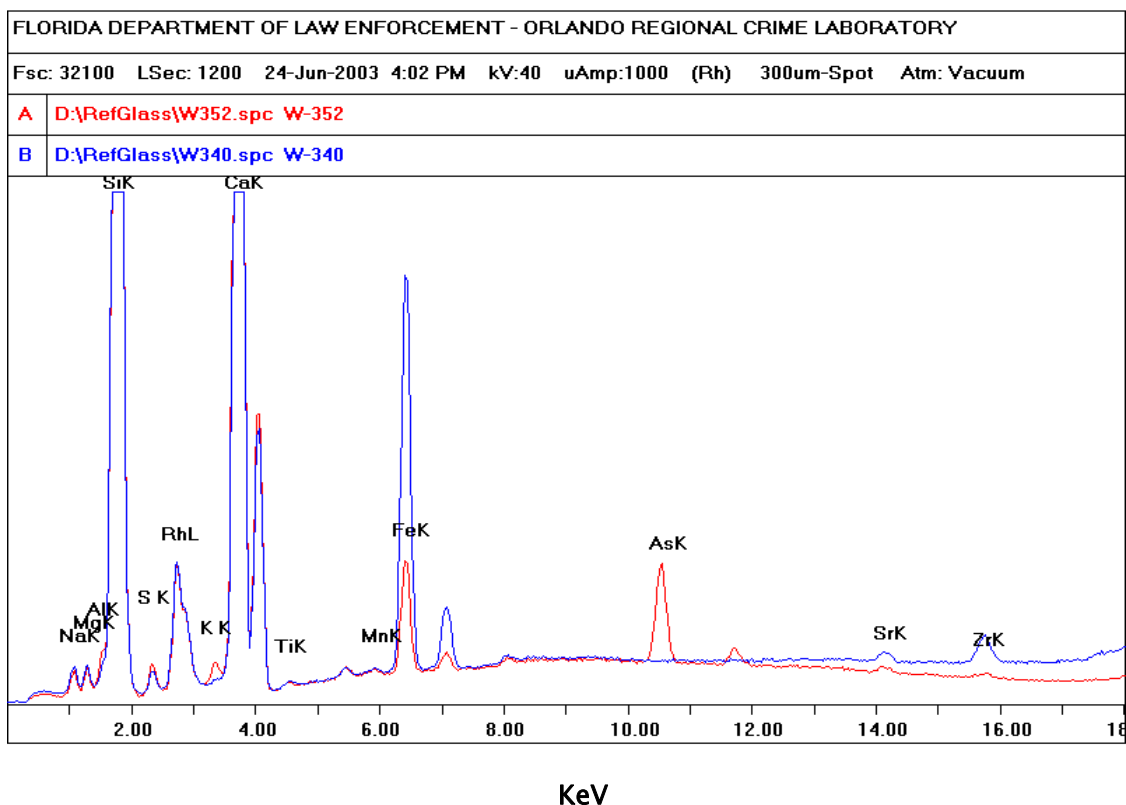
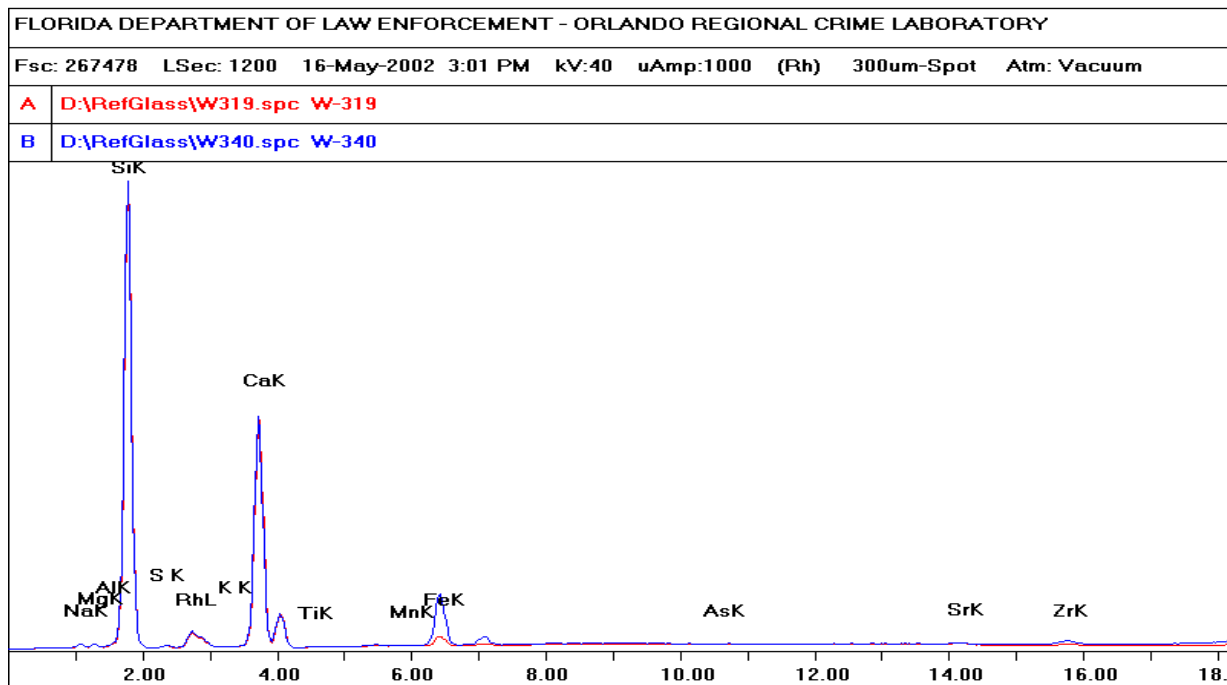
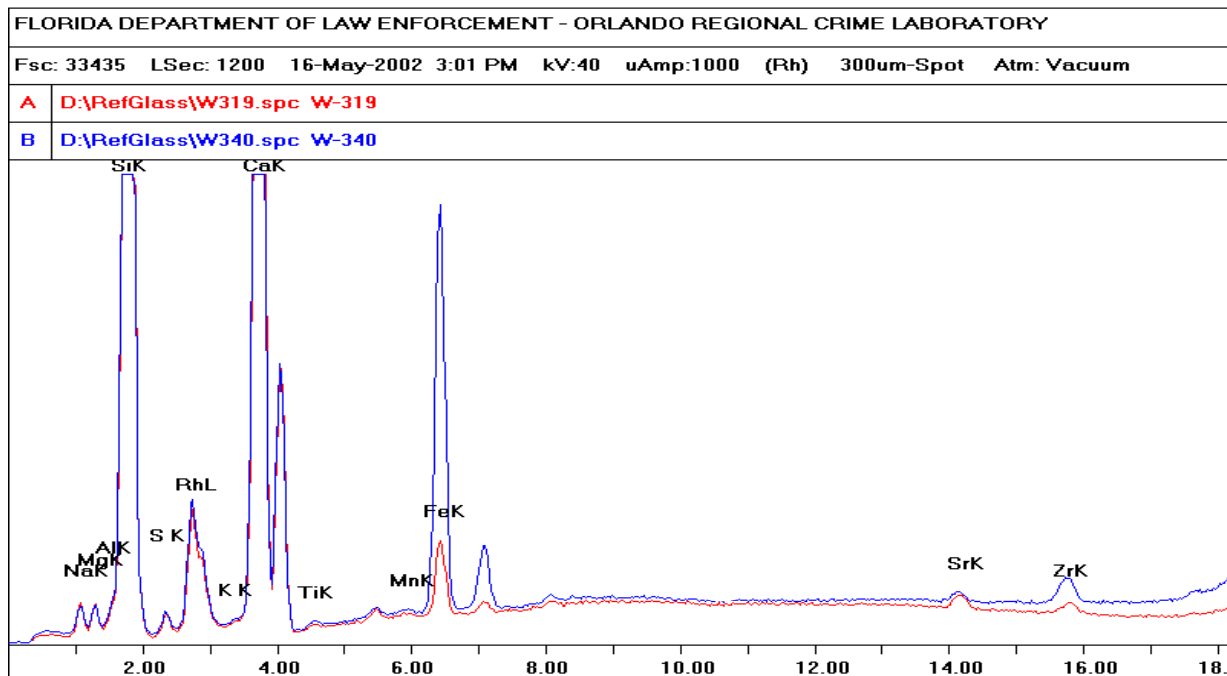
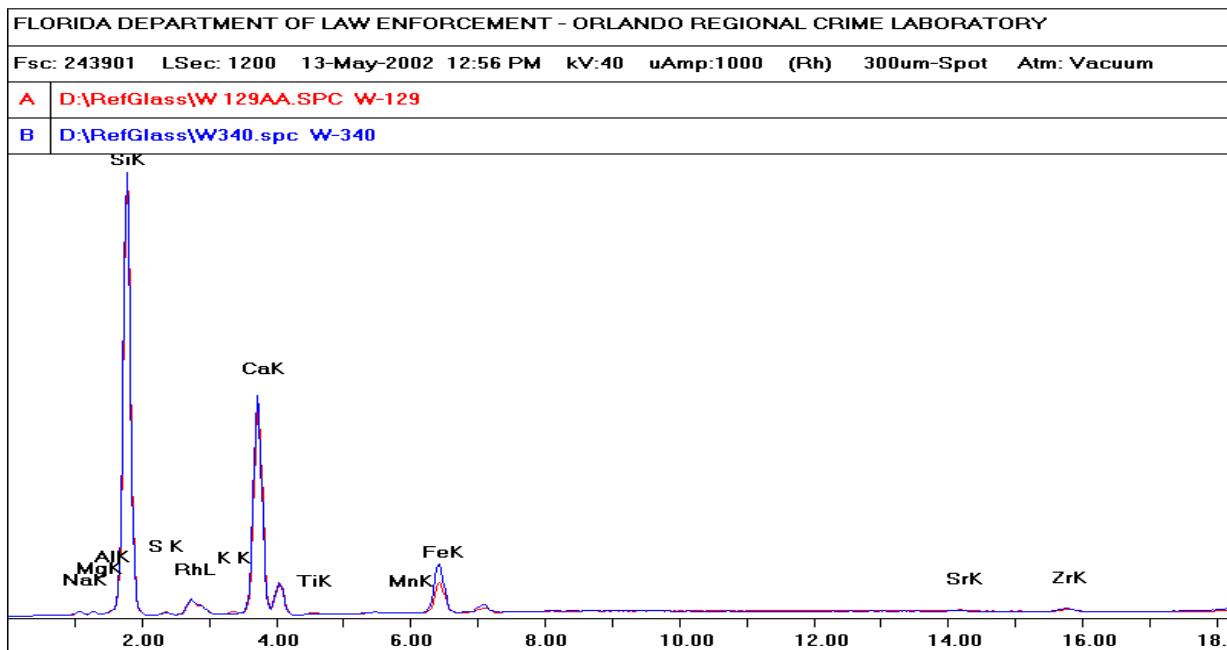
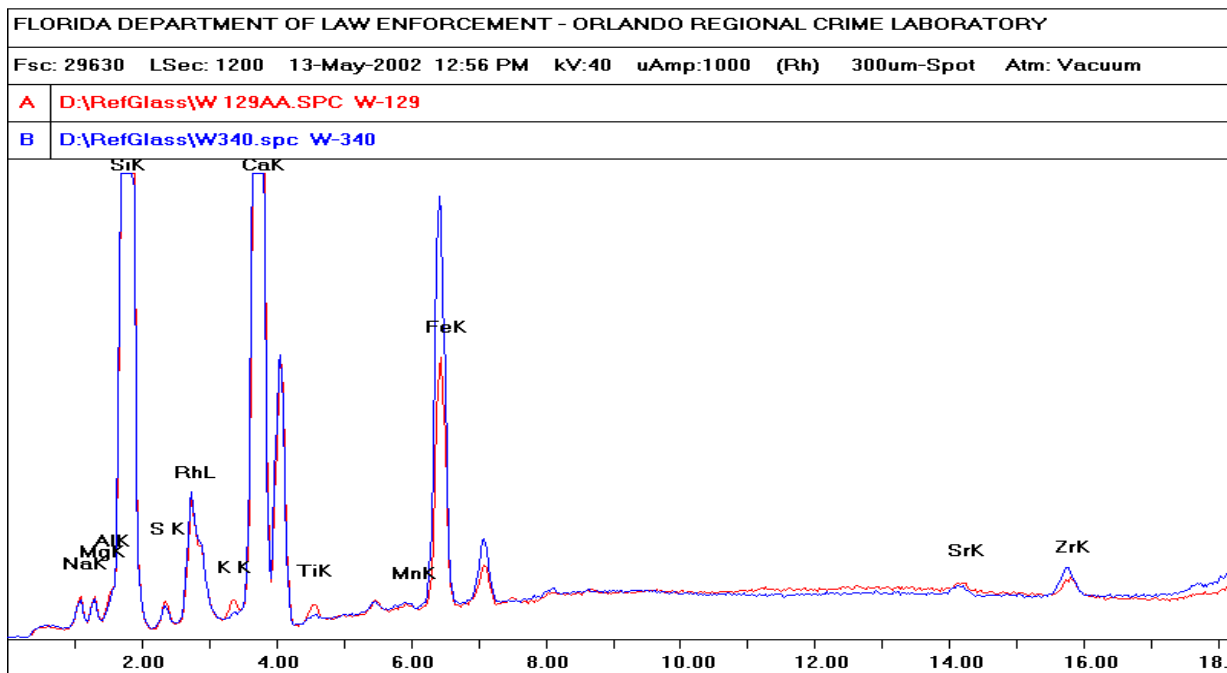


Figure 2: Samples W340 and W319 from Set 1 demonstrate semi-quantitative differences in their levels of Fe and Zr. The spectra are normalized to the most intense peak (Si K α) with the lower spectra displayed at full scale intensity and the upper spectra displayed with an expanded scale to visualize trace components.



KeV

Figure 3: Samples W340 and W129 from Set 1 demonstrate semi-quantitative differences in their Ca/Fe, Ca/K and Fe/Ti peak intensity ratios. The slight apparent differences in the Sr/Zr ratios are indistinguishable using a +/- 3 standard deviation criterion for three replicates of each sample. The spectra are normalized to the most intense peak (Si K α) with the lower spectra displayed at full scale intensity and the upper spectra displayed with an expanded scale to visualize trace components.



KeV

Glass Refractive Index Measurement System

Samples were cracked and five fragments were selected from each. Each of the five fragments was re-cracked and the refractive index was measured on three edges of each at 589 nanometers using a Foster + Freeman GRIM 2² system and the oil immersion technique. Locke B silicone oil³ was used as the mounting medium and was calibrated using a series of Locke B glass reference standards³. The accuracy of the oil's refractive index calibration was subsequently checked using two external glass standards, NIST Standard Reference Material 1822⁴ and the Locke B-5 glass standard³. The Locke B-5 standard was not used in creating the oil calibration curve. The mean of the fifteen measurements and their standard deviations were recorded for each. The means of each of the possible pairs were inter-compared using a variety of discrimination criteria, including ± 2.5 times the standard deviation, ± 2.0 times the standard deviation, a fixed criterion of ± 0.00010 , range overlap, and the T-test with Welch modification (assuming unequal variance) using both 99 percent and 95 percent confidence levels. The latter two were calculated on Microsoft Excel⁵ and are the most aggressive of the suite.

Micro X-ray Fluorescence Spectrometry

Newly cracked samples were washed in acetone and laid on the surface of a sheet of X-ray analysis film⁶ stretched over an open aperture and held in place by a very small amount of contact adhesive⁷. Irregular shaped samples were positioned with the flattest bulk glass fractured surface (not original surfaces) facing upward using the contact adhesive as an aid in positioning. Three to five separate fragments were analyzed for each sample. In the first set of 37 samples three separate fragments were analyzed for most samples and five for some (those demonstrating elevated relative standard deviations for the Ca/Fe or Sr/Zr ratios) while in the second set of 30 samples five separate fragments were analyzed for each sample.

³ Locke Scientific Services Ltd., The Old Laundry Bridge Street, Southwick, Fareham, PO17 6DZ, UK.

⁴ National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA.

⁵ Microsoft Corporation, One Microsoft Way, Redmond, WA 98052, USA.

⁶ Kapton Polyimide X-ray film, 7.5 micron thickness, Chemplex Industries Inc., 2820 SW 42nd Ave. Palm City, FL 34990-5573, USA.

⁷ Liquid Paper Dry Line transfer contact adhesive, Sanford, a Division of Newell Rubbermaid, 2707 Butterfield Road, Oak Brook, IL, 60523, USA.

Analyses were performed on an EDAX Eagle II micro X-ray fluorescence spectrometer⁸ equipped with a Rhodium X-ray tube and 300 micron mono-capillary focusing optic under vacuum. The tube was run at a potential of 40kV with the current adjusted to provide a dead time of approximately 40 to 45 percent. The Beryllium windowed Si(Li) energy dispersive X-ray detector was operated at a 17 microsecond processing time constant collecting data for 1200 live seconds. One relatively flat area was targeted for analysis on each of the three to five replicates. Spectra were plotted at two attenuations for each analysis permitting visual comparison of both the high and low intensity peaks. The spectral data was also processed using EDAX software⁸ for background subtraction, peak deconvolution, and peak intensity calculation. The peak intensity ratios and standard deviations for the replicates were recorded for Ca/Fe, Sr/Zr, Ca/Mg, Ca/K, Fe/Zr, Fe/Sr, and Fe/Ti and inter-compared in a pair-wise fashion using both a ± 3 times the standard deviation criterion and a T-test with Welch modification (assumed unequal variance) at a 95 percent confidence level.

RESULTS AND DISCUSSION

A summary of the results of inter-comparisons of the refractive indices for the initial twenty-one samples of Sample Set 1 using a variety of discrimination criteria can be found in Table 3. While 93 percent of the 210 possible pairs are indistinguishable using the ± 2.5 standard deviation criterion, only 37 percent of them were found to be indistinguishable using the aggressive T-test criterion at a 95 percent confidence level. It is indeed striking to see the wide spread of discrimination power provided by simply choosing different discrimination criterion. This speaks strongly for the need to develop a national consensus on the appropriate criterion. Much has been written on this topic over the years, with Bennett, et. al. (9) most recently cautioning on the use of parametric statistical methods given evidence that refractive index in a window is not normally distributed. They further demonstrate that acquisition of a truly representative standard is quite difficult, even if the analyst has the entire window at his/her disposal. Considering the more conservative ± 2.5 standard deviation criterion (equivalent to a 97.5 percent confidence level), most of the samples chosen to have similar nominal refractive indices do indeed appear to be indistinguishable.

Pair-wise inter-comparison of the μ -XRF results for the 666 possible pairs in Set 1 using spectral overlay and ± 3 standard deviation criteria discriminates all but three of the pairs (W142/W143, W319/W320, and W23/W323). Two of these three pairs are inside/outside panes of the same laminated windows. Application of the T-test as described above permits further discrimination of the W23/W323 pair. These two approaches yield discrimination powers of 99.5 percent or better on this set of

⁸ EDAX Inc., part of AMETEK, Inc., Materials Analysis Division, 91 McKee Drive, Mahwah, New Jersey, 07430, USA.

randomly acquired flat glass samples having similar refractive indices. The W142 and W143 glass samples also served as controls in this study since they were found to be indistinguishable in the previously reported exercise using the first twenty-one samples of Set 1 (7).

Table 3: Discrimination power of various refractive index criteria for the first twenty-one samples in Set 1 using Foster + Freeman GRIM (210 possible pairs)

Criterion	Number Indistinguishable Pairs	Percent Indistinguishable
+/- 2.5 Standard Deviation	196	93
+/- 2.0 Standard Deviation	174	83
+/- 0.00010 Fixed Criterion	126	60
Range Overlap	176	84
T-test with Welch modification at 99% confidence level	120	57
T-test with Welch modification at 95% confidence level	78	37

Pair-wise inter-comparison of the μ -XRF results for the 435 possible pairs in Set 2 using spectral overlay and +/- 3 standard deviation criteria discriminates all but eight of the pairs (W234/W235, W393/W394, W234/W393, W234/W394, W235/W393, W235/W394, W252/W295, and W98/W213). Six of the pairs resulted from the four indistinguishable samples W234, W235, W393 and W394 that come from two separate laminated windows, where W234/W235 and W393/W394 are inside/outside panes of each window. Application of the T-test as described above permits further discrimination of the eight pairs leaving only the W234/W235 and W393/W394 pairs indistinguishable. This yields discrimination powers of approximately 98.0 to 99.5 percent respectively on this second set of randomly acquired flat glass samples having similar refractive indices.

As reported by Howden et. al. and Dudley et. al. (10, 11), X-ray fluorescence spectrometry analyses of small glass fragments are prone to reduced precision as a result of critical depth effects and variation in take-off angle effects. The samples analyzed in the previous two sets were infinite thickness with respect to X-ray penetration. That is, if the samples compared are thicker than approximately 1.5 millimeters, little to no critical depth effects are experienced (12). In order to evaluate the impact of sample thickness on discrimination power, small (on the order of 1 millimeter) thin samples of the initial set of twenty-one samples in Set 1 were also compared by μ -XRF for the previously reported study (7). Using the more conservative spectral overlay and +/- 3 standard deviation criteria, eleven of the 210 possible pairs

were found to be indistinguishable resulting in a discrimination power of approximately 95 percent.

CONCLUSION

This study corroborates the previously reported improved discrimination power afforded by trace elemental comparisons using μ -XRF in addition to refractive index comparisons. For each set of sheet glasses having quite similar refractive index ranges, 98.0 to 99.5 percent of the thicker sample pairs were discriminated by μ -XRF. This discrimination power is slightly reduced as samples become quite thin or their surfaces become markedly uneven. Hence, only 95 percent of smaller thin sample pairs from one subset were discriminated. The results demonstrate that despite these limitations, μ -XRF remains a very robust non-destructive technique in the discrimination of glass samples encountered in typical forensic casework.

ACKNOWLEDGEMENTS

I would like to thank Ted Berman, Kari Lavoij, and Kathleen Mazek who shared in the many hours of analysis and data evaluation. Special thanks to Ted Berman, Troy Ernst, David Green, Marianne Hildreth, Chip Pollock, and Jan Taylor for their time and knowledge in review of and suggestions to the original draft. And a final thank you to the Florida Department of Law Enforcement for granting the time and instrumentation hours to evaluate the samples.

REFERENCES

1. SWGMAT Forensic Glass Examinations Guidelines. Forensic Science Communications, (2005) 7:1.
2. Koons, R. D., Buscaglia, J., Bottrell, M., and Miller, E. T. Forensic glass comparisons. In: *Forensic Science Handbook*. 2nd ed. R. Saferstein, ed. Prentice-Hall, Upper Saddle River, New Jersey (2002) 1:161-213.
3. Almirall, J. Elemental analysis of glass fragments. In: *Trace Evidence Analysis and Interpretation: Glass and Paint*. B. Caddy, ed. Taylor and Francis, London (2001) 65-83.
4. Buscaglia, J. Elemental analysis of small glass fragments in forensic science. *Analytica Chimica Acta* (1994) 288:17-24.
5. Personal communications, National Institute of Justice sponsored Elemental Analysis Working Group, coordinated by the International Forensic Research Institute,

Department of Chemistry and Biochemistry, Florida International University, Miami, Florida (2008 to 2010).

6. Hicks, T., Sermier, F. M., Goldmann, T., Brunelle, A., Champod, C., Margot, P. The classification and discrimination of glass fragments using non destructive energy dispersive X-ray microfluorescence. *For. Sci. Int.* 137 (2003) 107–118.
7. Umpierrez, S., Castro, W., Ryland, S., Almirall, J.R. Forensic elemental analysis of glass by laser induced breakdown spectroscopy (LIBS), electron microprobe (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and X-ray fluorescence spectrometry (XRF). Presented at the American Academy of Forensic Sciences 57th Annual Meeting, New Orleans, Louisiana, February 21–26, 2005.
8. Naes, B. E., Umpierrez, S., Ryland, S., Barnett, C., Almirall, J.R. A comparison of laser ablation inductively coupled plasma mass spectrometry, micro X-ray fluorescence spectroscopy, and laser induced breakdown spectroscopy for the discrimination of automotive glass. *Spectrochimica Acta, Part B* 63 (2008) 1145–1150.
9. Bennett R.L., Kim, N.D., Curran, J.M., Coulson, S.A., Newton, A.W. Spatial variation of refractive index in a pane of float glass. *Sci. Justice* (2003) 43:2:71–76.
10. Howden, C.R., Dudley, R.J., Smalldon, K.W. The analysis of small glass fragments using energy dispersive X-ray fluorescence spectrometry. *J. Forens. Sci. Soc.* (1978) 18: 99–112.
11. Dudley, R. J., Howden, C. R., Taylor, T. J., and Smalldon, K. W. The discrimination and classification of small fragments of window and nonwindow glasses using energy-dispersive X-ray fluorescence spectrometry. *X-Ray Spectrometry* (1980) 9:119–122.
12. Seaman, A. X-ray Fluorescence Spectrometry ACS Short Course, 51st Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Morial Convention Center, New Orleans, Louisiana, March 12–17, 2000.