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Elemental Analysis by Energy Dispersive X-Ray: A Significant Factor in the Forensic Analysis of Glass

Comparison of glass particles by the forensic scientist is routinely accomplished by measuring some physical properties. Direct comparison of densities ϱ and refractive indexes (η_C, η_D, and η_F being the refractive indexes determined at 6563, 5893, and 4861 nm, respectively) are the most widely used physical measurements because of convenience, reproducibility, sensitivity, and applicability to small sample size. Traditionally, if the physical comparison showed significant difference, it was concluded that the two glass samples could not have had a common origin. Conversely, when the specimens were not distinguishable the forensic scientist reported these samples as possibly having the same origin. Generally he did this without giving consideration to another variable—elemental composition of the samples.

M. D. G. Dabbs' article [*1*] illustrates that trace element analysis has further characterized a group of modern production window glasses that were indistinguishable on the basis of refractive index and density. In our study, energy dispersive X-ray spectrometry (EDX) was used for the elemental analysis of glass samples. This analytical technique has not seen widespread use in forensic science laboratories because of cost and complexity; consequently, the use of EDX has been limited to a few larger facilities.

The physical properties of density and refractive index reflect only the elemental composition of multicomponent solutions such as glass on an averaging basis. Quality control in the glass industry is routinely monitored by refractive index. Consequently, within the limits of common glass formulations there is little control or knowledge of elemental composition, which can be a highly variable factor and should be examined when forensic science glass comparisons are the objective. There are two possible advantages for doing this: (a) the glass samples may be further characterized and (b) they may in fact be distinguishable even though they possess the same physical properties. Dabbs and coworkers established the need for elemental analysis. The EDX analysis of glass reported in this article substantiates their findings.

Method

The following glass samples were examined with respect to density, refractive index and elemental composition.

A. An 18 by 24-in. (0.46 by 0.61-m) pane of window glass. The elemental composition was measured in nine specific locations on the pane (Fig. 1);

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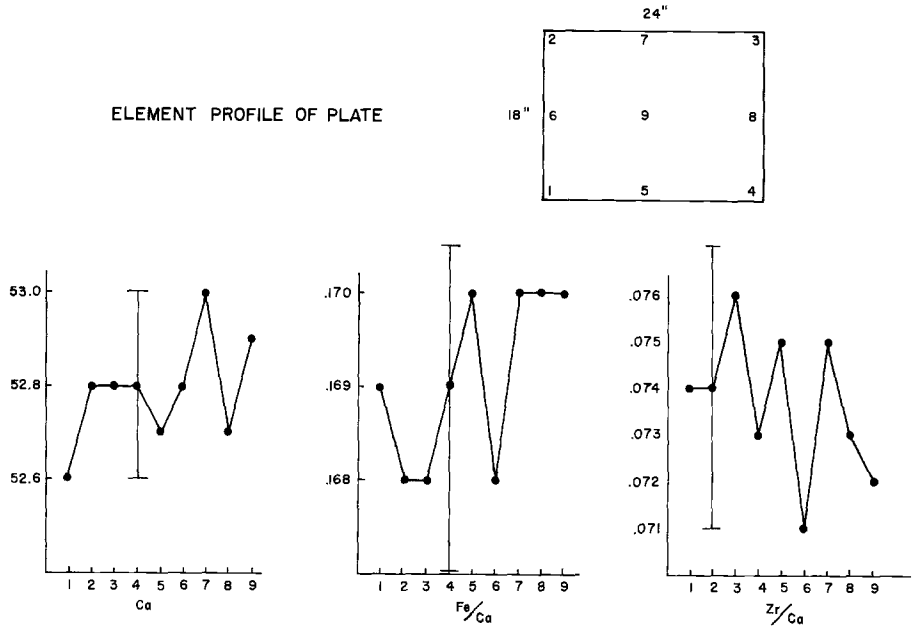


FIG. 1—*Variation in elemental analysis as determined on a pane of plate window glass.*

B. Twenty-four samples of window glass from successive production batches of sheet glass from Pittsburg Industries Ltd. (P.I.T.) and sheet and float glass from Pilkington Bros. Ltd. (PILK) (Figs. 2-6 and Table 1);

C. Fifty-two window glasses acquired as comparison window glass from casework previously classified by Fong [*2*] (Figs. 7-13 and Table 2);

D. Three window glass samples from an actual case, indistinguishable with respect to dispersion curves and density (Figs. 14, 15 and Table 3, Samples K1, K6, and K13); and

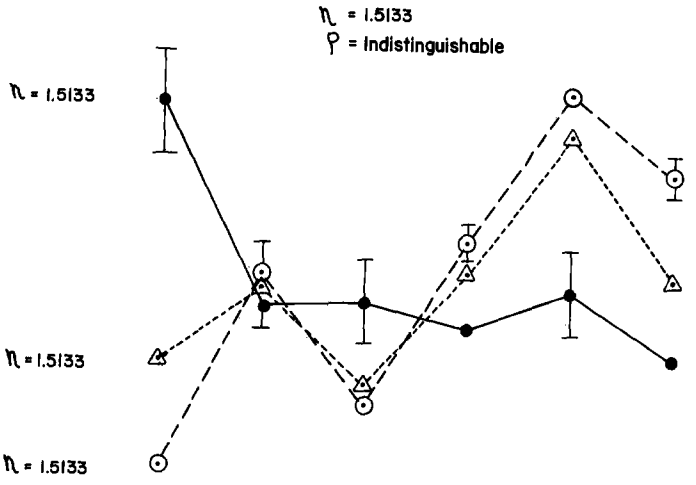


FIG. 2—*Elemental net ratios of three samples of Pilkington Bros. plate glass that are indistinguishable by physical properties.*

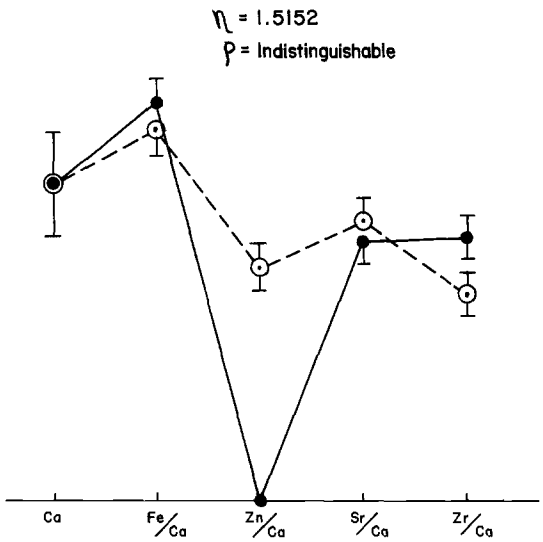


FIG. 3—*Elemental net ratios of samples of Pilkington Bros.* (open circle) *and Pittsburgh Industries Ltd.* (solid circle) *plate glass indistinguishable by physical properties.*

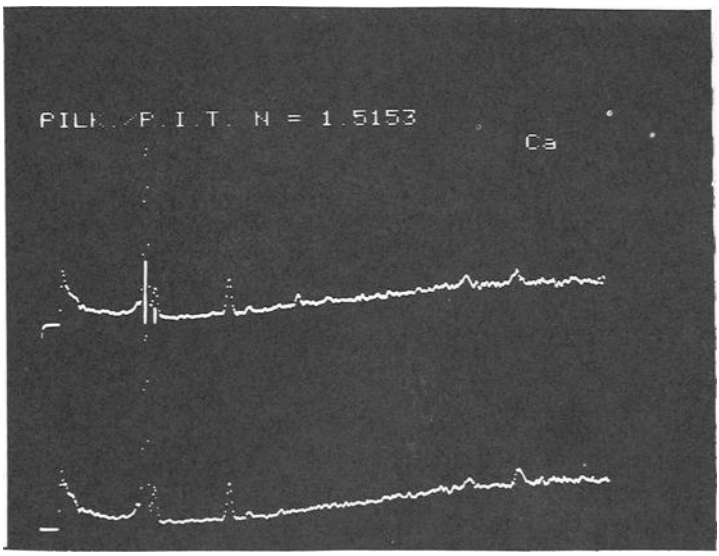


FIG. 4—*Cathode ray tube (CRT) display of the elemental composition of samples of Pittsburgh Industries Ltd. and Pilkington Bros. plate glass indistinguishable by physical properties.*

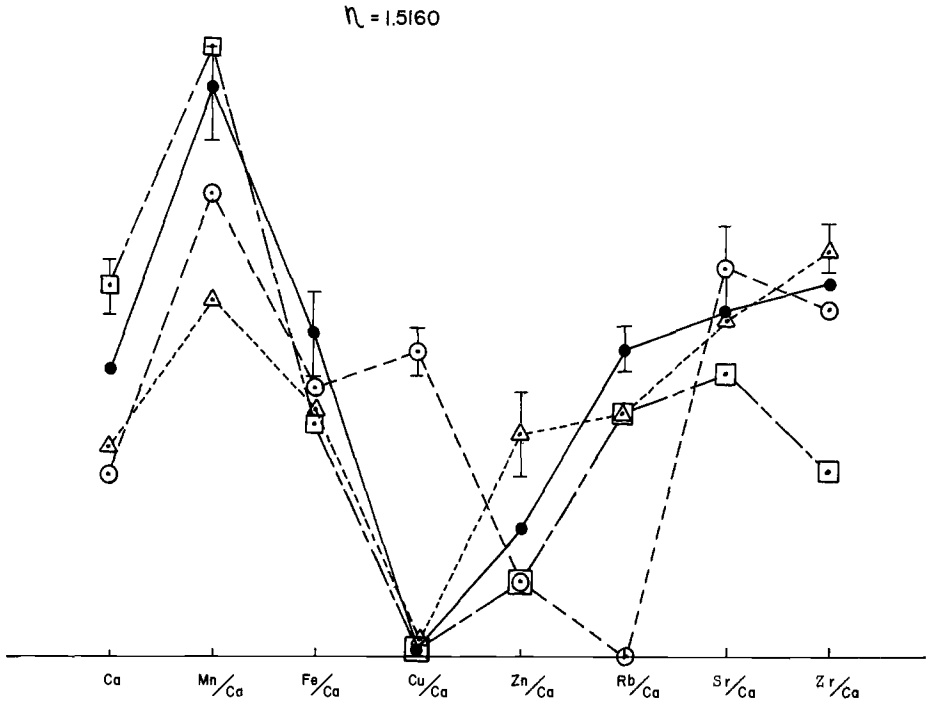


FIG. 5—*Elemental net ratios of four plate glass samples from Pilkington Bros. indistinguishable by refractive indexes.*

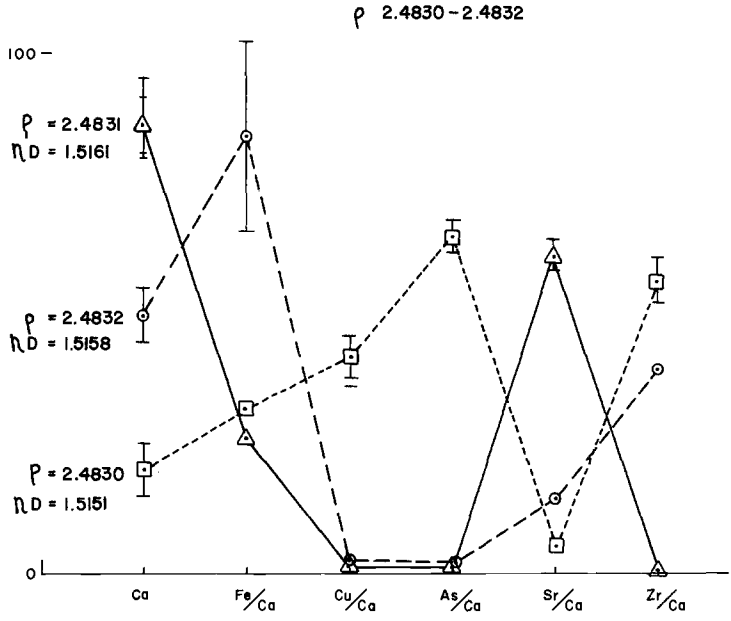


FIG. 6—*The elemental, density, and refractive index variation in three window glass samples.*

TABLE 1—*Net ratios of elements in window glass from our samples.*

Manufacturer[a]	Sample[b]	η_D	Ca (100) ±1	Mn/Ca ±0.002	Fe/Ca ±0.009	Cu/Ca ±0.002	Zn/Ca ±0.004	As/Ca ±0.016	Rb/Ca ±0.002	Sr/Ca ±0.0016	Zr/Ca ±0.008
PILK	12[b]	1.5133	45	0	0.115	0	0.008	0.517	0	0.046	0.153
PILK	13[b]	1.5133	52	...	0.103	...	0.013	0.431	...	0.027	0.082
PILK	14[b]	1.5133	47	...	0.110	...	0.009	0.489	...	0.042	0.113
PIT	9	1.5151	56	...	0.182	...	0.008	...	...	0.451	...
PIT	8[b]	1.5152	57	...	0.148	...	...	...	...	0.049	0.100
PILK	11[b]	1.5152	57	...	0.141	...	0.044	...	...	0.053	0.078
PILK	6	1.5153	52	...	0.192	...	0.057	...	...	0.055	0.090
PIT	7	1.5153	59	...	0.143	...	0.006	...	...	0.057	0.066
PIT	8[b]	1.5153	57	...	0.163	...	0.003	...	...	0.055	0.111
PILK	9[b]	1.5153	54	0.017	0.182	...	0.068	...	...	0.099	0.126
PILK	10	1.5155	59	...	0.178	...	0.062	...	...	0.067	0.097
PILK	7	1.5155	53	...	0.182	...	0.049	...	...	0.081	0.118
PIT	5	1.5156	62	...	0.149	...	...	...	...	0.051	0.055
PIT	4	1.5157	55	...	0.153	...	...	...	...	0.058	0.099
PILK	4[b]	1.5160	54	0.017	0.197	...	0.021	...	0.023	0.032	0.077
PILK	5[b]	1.5160	57	0.027	0.211	...	0.012	...	0.029	0.033	0.071
PILK	5(a)[b]	1.5160	53	0.022	0.201	0.029	0.007	...	...	0.037	0.066
PILK	6[b]	1.5160	60	0.029	0.194	...	0.007	...	0.023	0.027	0.035
PILK	2	1.5161	51	0.016	0.157	...	0.038	...	...	0.050	0.126
PILK	3	1.5161	57	0.020	0.210	...	0.006	...	0.018	0.042	0.060
PILK	1	1.5162	55	0.027	0.209	...	0.010	...	0.011	0.032	0.058
PIT	3	1.5165	58	...	0.166	...	0.058	...	0.010	0.170	0.145
PIT	2	1.5166	61	...	0.151	...	0.044	...	0.039	0.159	0.111
PIT	1	1.5252	78	...	0.109	...	...	...	...	0.146	0.120

[a] PILK = Pilkington Bros. Ltd.; PIT = Pittsburgh Industries Ltd.
[b] Indicates samples plotted in Figs. 2–6.

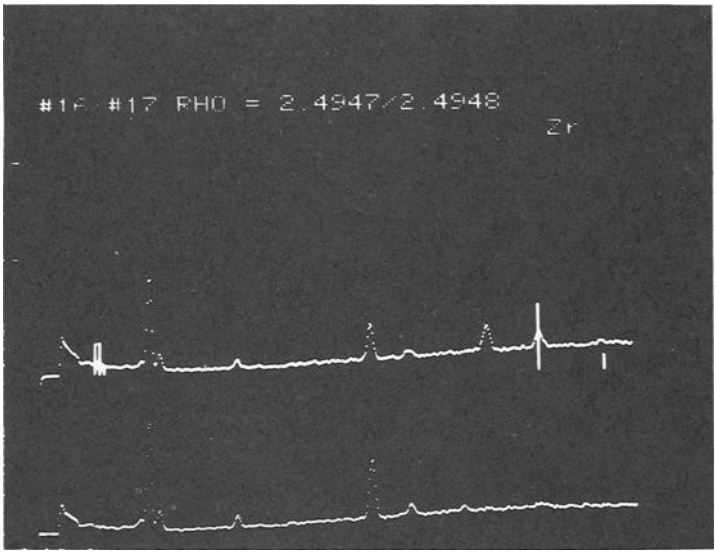


FIG. 7—*CRT display of elemental spectra of two window glass samples in the density population 2.4943–2.4948.*

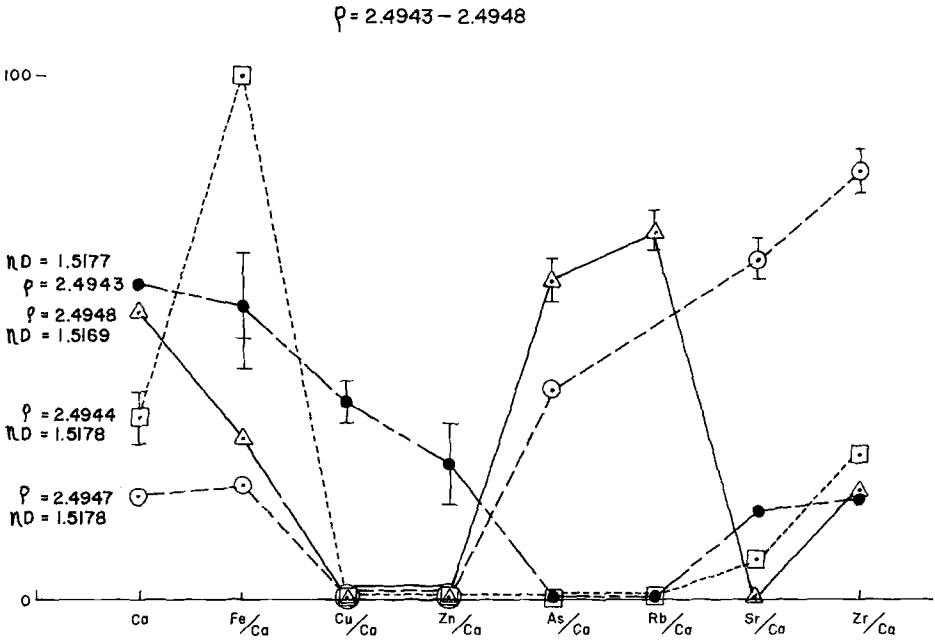


FIG. 8—*Elemental net ratios of the four window glass samples in the density population 2.4943–2.4949.*

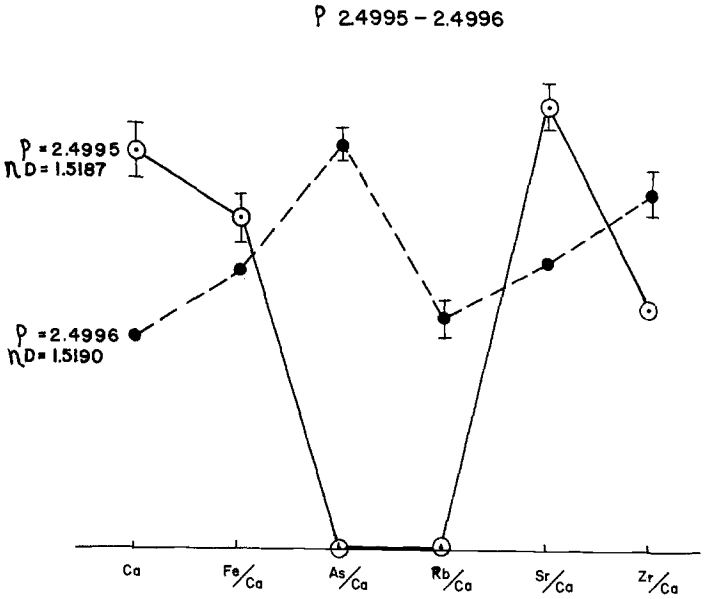


FIG. 9—*Elemental net ratios of two window glass samples in the density population 2.4995–2.4996.*

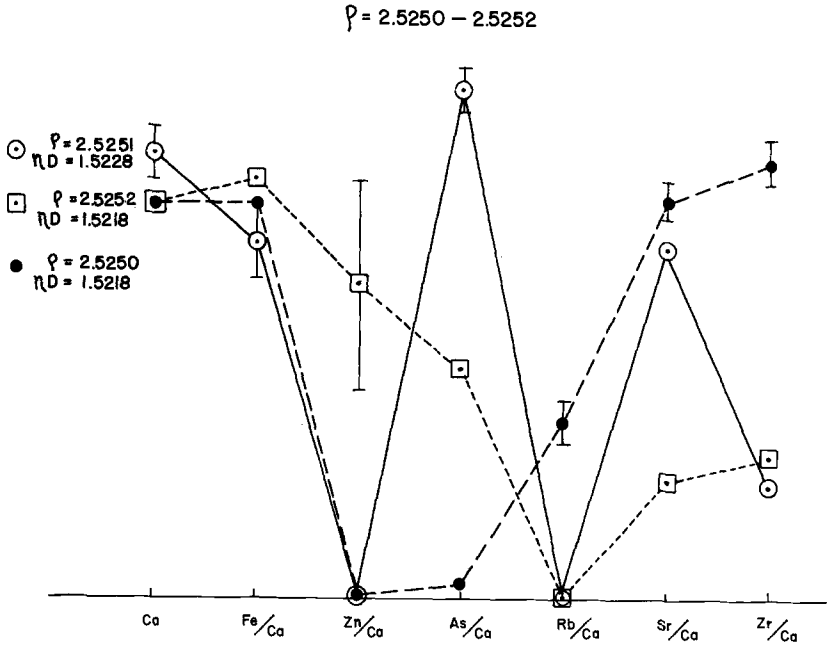


FIG. 10—*Elemental net ratios of three window glass samples in the density population 2.5250–2.5252.*

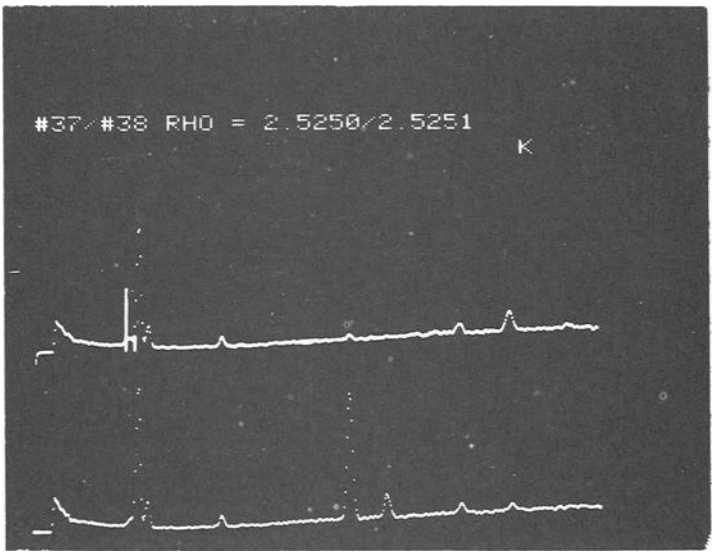


FIG. 11—*CRT display of the elemental spectra of two window glass samples in the density population 2.5250–2.5251.*

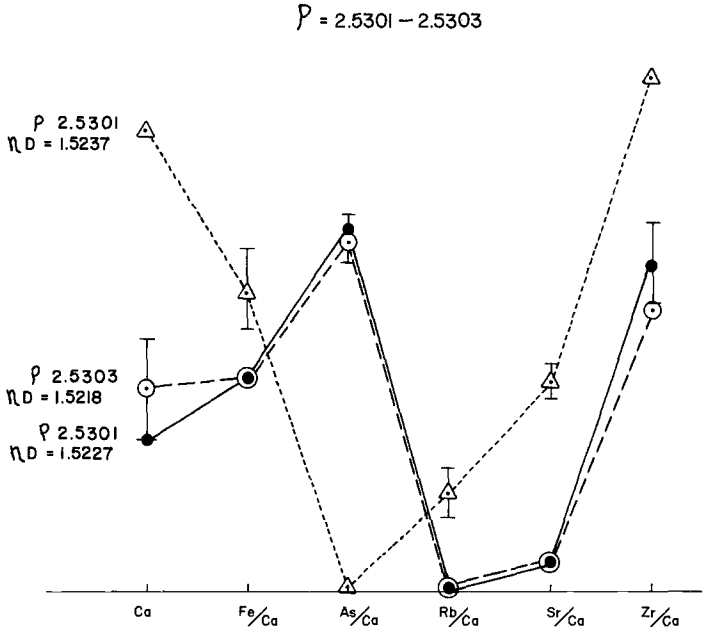


FIG. 12—*Elemental net ratios of three window glass samples in the density population 2.5301–2.5303.*

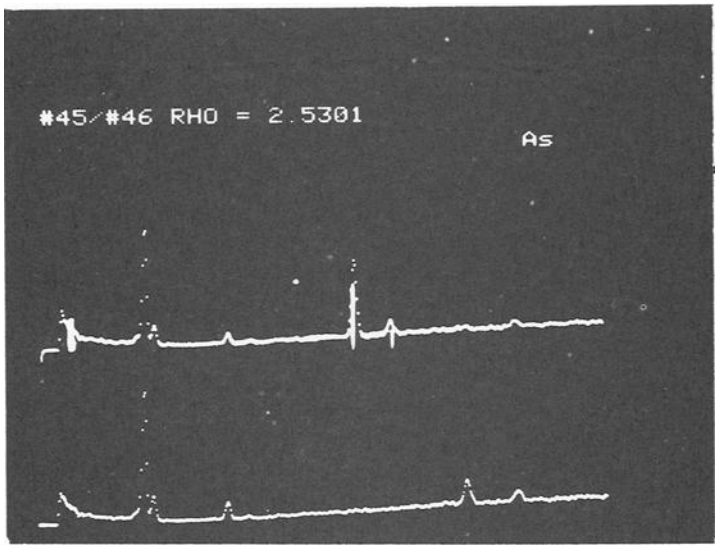
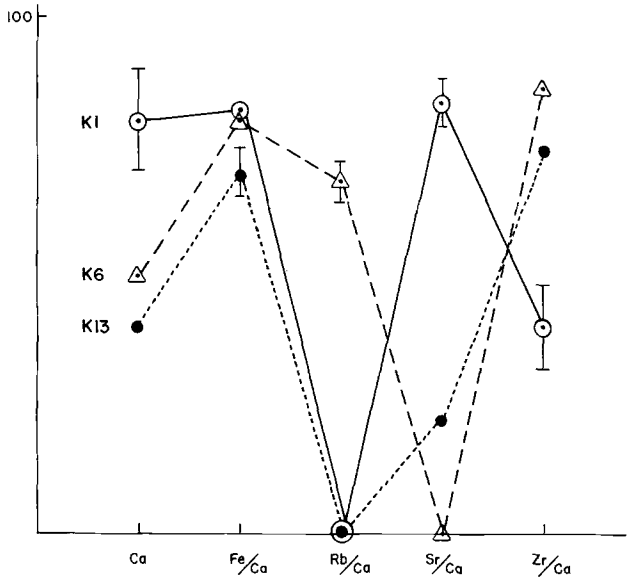


FIG. 13—*CRT display of elemental spectra of two window glass samples in the density population 2.5301–2.5303.*



	η_C	η_D	η_F	ϱ
K1	1.5143	1.5170	1.5236	2.479
K6	1.5140	1.5166	1.5234	2.476
K13	1.5135	1.5164	1.5232	2.474

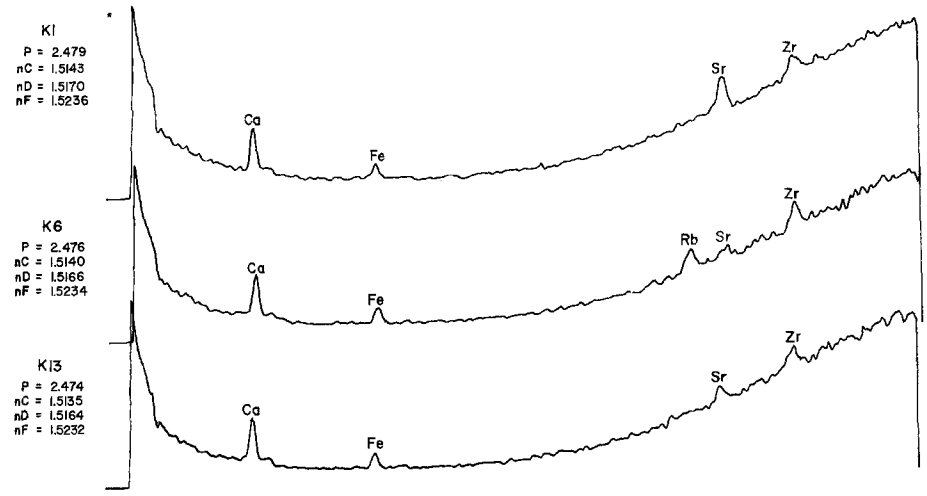
FIG. 14—*Glass samples from a burglary investigation. Samples were indistinguishable by physical properties alone. Samples were supplied by Dr. I. C. Stone of the Southwestern Forensic Institute.*

TABLE 2—*Net ratios of elements previously compared by Fong* [2] *for densities and now re-examined by EDX.*

Fong's Sample No.	ϱ	Ca (100) ±1	Ti/Ca	Mn/Ca ±.002	Fe/Ca ±0.009	Cu/Ca ±0.002	Zn/Ca ±0.004	As/Ca ±0.016	Rb/Ca ±0.002	Sr/Ca ±0.0016	Zr/Ca ±0.008
1	2.4821	55	0.010	0.009	0.150	...	...	...	...	0.029	0.124
2[a]	2.4830	46	...	...	0.126	0.021	...	0.646	...	0.017	0.140
3[a]	2.4831	59	...	...	0.123	...	...	...	...	0.245	...
4[a]	2.4832	52	...	...	0.152	...	...	...	...	0.059	0.099
5	2.4882	56	...	...	0.145	0.043	...	...	0.049	0.060	0.045
6	2.4883	49	...	...	0.086	...	...	1.226	...	0.101	0.086
7	2.4883	52	...	...	0.071	...	...	1.148	...	0.100	0.092
8	2.4885	81	...	...	0.084	...	...	...	...	0.569	...
9	2.4885	56	...	...	0.150	...	...	...	0.048	...	0.060
10	2.4899	58	...	...	0.163	...	...	...	...	0.073	0.036
11	2.4902	57	...	...	0.153	...	...	0.088	...	0.099	0.113
12	2.4903	52	0.012	0.023	0.128	0.018	...	0.103	...	0.056	0.091
14[a]	2.4943	62	0.004	...	0.116	0.019	0.013	...	...	0.083	0.049
15[a]	2.4944	57	...	...	0.160	...	...	...	...	0.036	0.068
16[a]	2.4947	54	...	...	0.082	...	...	0.403	...	0.323	0.202
17[a]	2.4948	61	...	...	0.091	...	...	0.605	0.035	...	0.051
18	2.4949	59	...	...	0.154	...	...	...	...	0.114	0.067
19	2.4972	69	0.009	...	0.042	...	...	0.036	...	0.148	0.095
20	2.4985	60	...	0.011	0.163	0.020	...	...	...	...	...
21	2.4990	54	...	...	0.183	...	...	...	...	0.039	...
22[a]	2.4995	59	...	...	0.156	...	...	...	...	0.082	0.092
23	2.4996	52	0.019	...	0.132	...	...	0.762	0.043	0.054	0.136
24	2.5002	71	0.008	...	0.053	...	...	0.026	...	0.124	0.099
25	2.5016	61	...	...	0.172	...	...	...	...	...	0.081
26	2.5019	61	...	...	0.198	...	...	0.593	...	0.074	0.076
27	2.5088	83	...	...	0.101	...	...	0.023	...	0.034	0.087
28	2.5115	80	...	...	0.110	...	...	0.018	...	0.089	0.072
29	2.5151	55	0.007	0.027	0.170	0.026	...	0.445	...	0.040	0.052
30	2.5184	63	...	...	0.126	...	...	0.567	0.030	0.026	0.052
31	2.5200	66	...	...	0.110	...	...	0.293	...	0.041	0.087
32	2.5206	72	...	...	0.109	...	...	0.333	...	0.037	0.088
33	2.5213	75	0.005	...	0.120	...	...	0.590	0.005	0.036	0.237
34	2.5215	72	...	...	0.139	...	...	0.591	...	0.049	0.083

35	2.5236	70	...	...	0.094	...	...	0.366	...	0.049	0.095
36	2.5249	79	...	...	0.103	...	...	0.541	0.043	0.066	0.042
37[a]	2.5250	75	...	...	0.076	...	...	0.034	0.017	0.076	0.209
38[a]	2.5251	85	...	...	0.068	...	...	0.972	...	0.067	0.055
39[a]	2.5252	75	...	...	0.080	...	0.006	0.420	...	0.023	0.068
40	2.5259	74	...	...	0.095	...	...	0.013	...	0.046	0.077
41	2.5288	80	...	...	0.121	...	...	...	...	0.238	0.114
42	2.5294	75	...	0.014	0.081	...	0.016	0.691	...	0.014	0.055
43	2.5294	82	...	...	0.130	...	...	...	...	0.085	0.134
44	2.5296	77	...	...	0.111	...	...	...	0.014	0.034	0.073
45[a]	2.5301	71	...	...	0.082	...	...	0.705	...	0.035	0.064
46[a]	2.5301	79	...	...	0.118	...	...	...	0.010	0.212	0.100
47[a]	2.5303	72	...	...	0.082	...	...	0.694	...	0.039	0.055
49	2.5310	79	...	...	0.136	...	...	...	...	0.282	0.109
49	2.5342	74	...	...	0.199	...	...	...	...	0.616	0.168
50	2.5358	100	0.007	0.004	0.071	...	...	...	...	0.041	...
51	2.5409	85	...	...	0.061	...	...	0.168	0.010	0.091	0.082

[a] Indicates samples plotted in Figs. 7–13.



	Ca Count	Fe/Ca Count	Rb/Ca Count	Sr/Ca Ratio	Zr/Ca Ratio
K1	1366	0.39	...	1.18	0.71
K6	1449	0.44	0.72	0.29	0.83
K13	1482	0.33	...	0.42	0.64

FIG. 15—*X-Y plots of the elemental spectra of the three glass samples shown in Fig. 14.*

E. Fifteen glass samples from a variety of case samples grouped according to their corresponding physical parameters (Figs. 16, 17 and Table 3, Samples 6, 7, and 8).

The samples were analyzed on a Finnigan Model 900 EDX system equipped with a 1-mm tin mini-collimator. Each sample was placed in the X-ray system aligned over the collimator and irradiated with X-rays, silver target, and 40 kV, 4 mA generator settings.

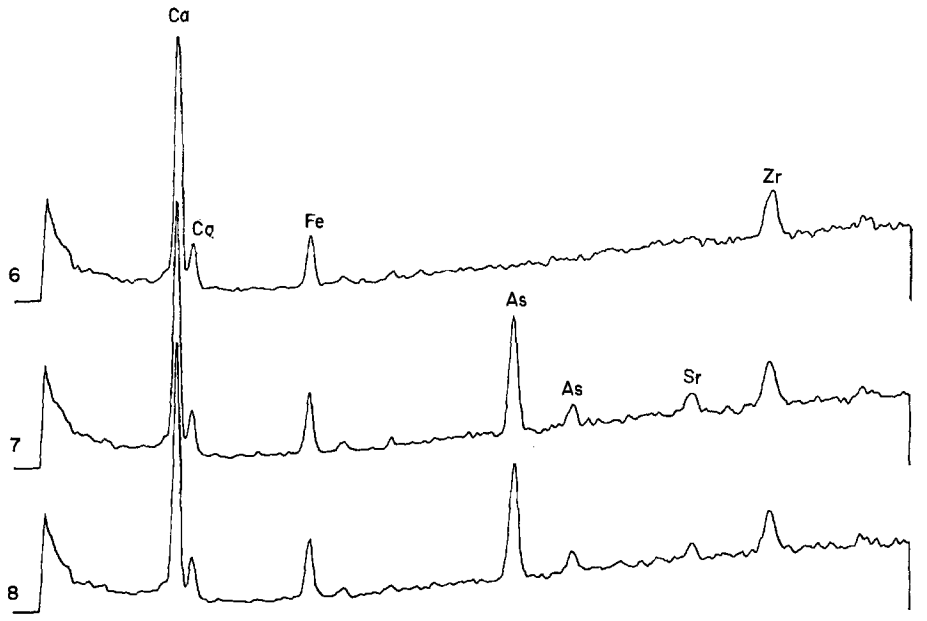
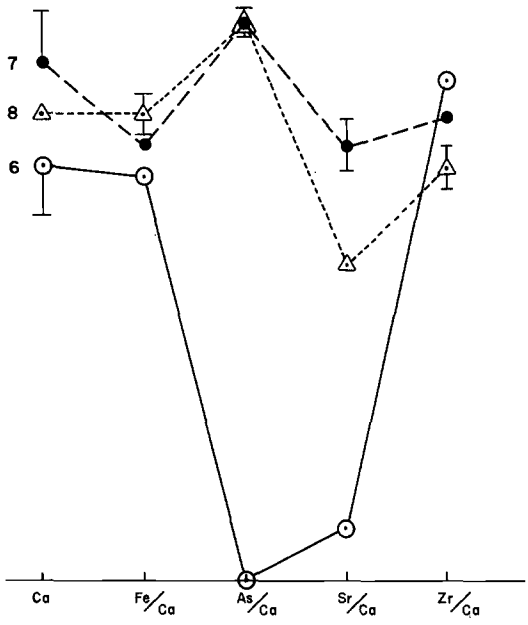


FIG. 16—*X-Y plots of the elemental spectra of three glass samples from selected cases investigated by the Federal Bureau of Investigation.*



	η_C	η_D	η_F	ϱ
6	1.5158	1.5183	1.5243	2.5046
7	1.5158	1.5184	1.5246	2.5040
8	1.5160	1.5184	1.5242	2.5046

FIG. 17—*Elemental net ratios of the three window glass samples supplied by the Federal Bureau of Investigation that were shown in Fig. 16.*

Counts were accumulated for 100 s and the preprogrammed system printed out net counts for the elements calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), arsenic (As), rubidium (Rb), strontium (Sr), and zirconium (Zr). Refractive indexes (η_D) of glass Samples B were measured on an Abbe refractometer. Refractive indexes (η_D) of Sample C were determined by using the temperature variation method and Mettler Hot Stage [3]. Dispersion curves and densities for Samples D and E were measured by Stone and Miller[4]. Densities of Samples B and C were measured by the authors.

Data Reduction

Samples A through E were analyzed by EDX. The calcium counts W in each sample were normalized to the highest calcium count found in the total glass population (16 000 counts = R) and put on a scale of 100. Analytical error in the normalized values (100 W/R) was determined to be ± 1 part in 100.

The net counts of the elements Mn, Fe, Cu, Zn, As, Rb, Sr, and Zr were ratioed to the Ca net counts in each sample to produce numerical values (Tables 1–3). These values with their associated 2-sigma variation are illustrated in Figs. 1–3, 5, 6, 8–10, 12, 14, and 17. The 2-sigma value associated with each net ratio is represented by a vertical bar with the top and bottom crossed with a short horizontal line. The sigma value was calculated as the square root value of the net counts [4] and the ratio of the average sigma value to the sigma value for Ca was calculated (Tables 1–3).

Specific glass samples were selected from those outlined in Tables 1–3 on the basis

[4] Personal communications.

TABLE 3—*Net ratios of elements in window glass indistinguishable in dispersion curves and density.*

Sample[a]	η_C	η_D	η_F	ϱ	Ca(100) ±1	Fe/Ca ±0.009	As/Ca ±0.016	Rb/Ca ±0.004	Sr/Ca ±0.004	Zr/Ca ±0.008
K1 [b]	1.5143	1.5170	1.5236	2.479	58	0.163	...	...	0.083	0.040
K6 [b]	1.5140	1.5166	1.5234	2.476	55	0.160	...	0.034	...	0.086
K13[b]	1.5135	1.5164	1.5232	2.474	54	0.139	...	...	0.022	0.074
6[c]	1.5158	1.5183	1.5243	2.5046	58	0.194	...	...	0.010	0.241
7[c]	1.5158	1.5184	1.5246	2.5040	60	0.211	0.486	...	0.084	0.223
8[c]	1.5160	1.5184	1.5242	2.5046	59	0.225	0.490	...	0.061	0.199

[a] Samples plotted in Figs. 14–17.
[b] These 3 samples are from 13 that could not be discriminated by physical properties.
[c] These 3 samples are from 15 that could not be discriminated by physical properties.

of similar density and refractive indexes. The elemental net ratios of the samples are graphically displayed in Figs. 2–4, 6, 8–10, 12, 14, and 17. The first graph (Fig. 1) illustrates the element profile on a single pane of window glass. The rectangle with numbers represents analysis points on the glass. The vertical bar in each graph represents the average 2-sigma value for each element. The point scatter for each element is within two standard deviations of the true value or the quality of statistical precision expresses a 95% confidence level. The results of this experiment establish that the variation of elemental composition across a pane of window glass is within the sigma variation of the experimental method. Glass samples illustrated in Fig. 2 are all from the same glass manufacturer, Pilkington Bros. They all have similar refractive indexes and are indistinguishable in density. The samples were removed from subsequent batches of glass. Two of the samples are fairly close in composition; however, one varies considerably in Ca and Zn/Ca, As/Ca, Sr/Ca, and Zr/Ca ratios.

Figure 3 displays glass samples from two different glass manufacturers, Pilkington Bros. and Pittsburgh Industries Ltd. These samples are indistinguishable by refractive indexes and by density. However, the samples can be differentiated on the basis of Zn/Ca ratio. Figure 4 demonstrates an elemental profile display of additional glass samples, one from Pittsburgh Industries and the other from Pilkington Bros. Both are indistinguishable by density and refractive indexes. However, the Sr/Ca ratios are different; the bottom spectrum contains a greater amount of Sr (P. I. T.). The top spectrum has traces of Zn in the sample (PILK), which also serves to characterize the two.

Figure 5 portrays four glass samples from Pilkington Bros. The samples fall into two distinct density groups but are indistinguishable by refractive indexes. In terms of their elemental compositions one of the samples (*open circle*) is quite different (Cu/Ca and Rb/Ca ratios). The other three are very similar with respect to elemental composition. However, one sample (*open square*) is differentiated on the basis of its Zr/Ca ratio.

The samples in Table 2 were compared by density and reported earlier by Fong [2]. These samples were re-examined by EDX and in those instances in which the samples correspond in density values, their refractive indexes were determined.

Figure 6 illustrates the elemental, density, and refractive index variations in three glass samples that Fong [2] could not differentiate by density alone, ϱ = 2.4830–2.4832. The elemental variations are considerable.

Two of the samples in density group 2.4943–2.4948 are illustrated with elemental spectra in Fig. 7. The corresponding elemental plots ϱ = 2.4943–2.4948 for the glass samples in Fig. 7 are illustrated by two of the line drawings (*open circle* and *open triangle*) in Fig. 8.

Another illustration of glass samples with similar physical qualities but decidedly different elemental compositions is displayed in Fig. 9. Figure 10 is a distribution of glass samples with densities ranging from 2.5250–2.5252. The samples can be classified into two sets by refractive indexes. However, two samples in the 1.5218 refractive index set cannot be differentiated on the basis of their physical parameters.

Spectra of samples of the 2.5250–2.5252 density range are displayed in Fig. 11. Their elemental compositions enable them to be separated easily from each other. Of particular interest is the presence of As in the bottom spectrum; it appears only as a trace in the top spectrum. Conversely, in the density range ϱ = 2.5301 to 2.5303 (Fig. 12), two of the glass samples fall into a distinct set, indistinguishable by density and elemental composition. However, these two samples are distinguishable by refractive indexes (*solid* and *open circles*).

Figure 13 illustrates the spectrum of the two distinct glass sets of Fig. 12, separated by density and elemental composition. The most apparent difference is that As is present in the two samples in the first set but not in the single sample.

Glass samples from a single burglary investigation were examined. Specimens K1, K6,

and K13 were the only samples that could not be eliminated by physical properties. The elemental net ratios of samples K1, K6, and K13 are graphically displayed in Fig. 14, whereas the samples' spectra are shown in Fig. 15. Fifteen glass samples from selected investigations were also examined. The spectra illustrated in Fig. 16 show the elemental composition of three of these glass samples. These samples were selected for their similarity with respect to physical properties. Figure 17 illustrates the elemental plots graphically. Note how Samples 6 and 8 are very similar in density and refractive indexes. However, the two samples are distinctly different with respect to their elemental compositions.

Conclusions

Eighty-one glass samples were analyzed by EDX; two were indistinguishable. However, when the physical properties of the glass samples were considered, all glass samples were distinguishable from each other.

The need to examine glass with respect not only to physical properties but also to elemental composition has been demonstrated. The authors believe that if glass is examined only by density and refractive indexes it is quite possible to conclude *incorrectly* that glass samples with the same physical qualities could have originated from the same source. To confirm that the glass specimens may have in fact originated from the same source their elemental compositions in addition to density and refractive indexes must be determined.

The analysis by EDX of glass samples can selectively eliminate most specimens on the basis of elemental differences. If this step is performed prior to refractive index or density measurements considerable time savings can be realized in casework situations.

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