

M. A. Haney,¹ Ph.D.

Comparison of Window Glasses by Isotope Dilution Spark Source Mass Spectrometry

Comparison of glass fragments in forensic work is commonly done by measurements of refractive index and density. These methods are particularly well-suited for flat glass such as in windows. Further differentiation has been shown feasible by elemental analysis. Neutron activation analysis (NAA) [1], spark source mass spectrometry (SSMS) [2], and energy-dispersive X-ray fluorescence (EDX) [3] have all been successful in differentiating window glasses having identical physical properties.

The present work applies the technique of isotope dilution spark source mass spectrometry (ID-SSMS) [4, pp. 283-291] to the elemental analysis of window glass fragments indistinguishable by physical properties alone. This technique has the unique advantage of yielding accurate, absolute elemental concentrations without the use of standards. Although unnecessary for direct comparison of evidence, absolute measurements enhance a forensic science program by enabling a data base to be accumulated. The data base provides a firm yardstick for comparison and allows independent judgment as to the value of the technique. In principle, of course, a standard can be used to obtain absolute measurements with any technique. In practice this is often difficult because of a lack of a suitable standard. It is particularly difficult to quantify with the EDX method.

Eight samples collected as evidence by the FBI Laboratory and 20 samples collected by the Orange County Sheriff's Coroner Crime Laboratory (California) were analyzed. Both refractive index and density were measured on the FBI samples, whereas only refractive index was measured on the Orange County samples. Samples from two window panes were also analyzed as a check on homogeneity.

Experimental Procedure

Large glass fragments were ground into a coarse powder in an agate vial on a Spex mixer/mill. Small fragments (~1 mm) were used directly with no grinding. The only purpose of the grinding is to facilitate dissolution of the sample.

About 10 mg of the sample was accurately weighed into a Teflon® beaker. The minimum sample size is presently limited to about 1 mg because of reagent blank. A total of 25 μ l of sulfuric acid (Baker Ultrex®) and 5 drops of hydrofluoric acid (Fisher ACS) were added. The beakers were warmed on the hot plate until dissolution occurred, about 5 to 10 min depending on the size of the fragments.

The dissolved samples were spiked with 50 to 500 μ l of separated isotope solutions. The concentration and volume of added isotope spikes were adjusted to give an isotopic ratio of approximately unity in the final solution. The separated isotopes were obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn., as salts of ⁴¹K, ⁵⁷Fe, ⁸⁷Rb,

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¹Research chemist, Scientific and Technical Services Division, Federal Bureau of Investigation, Washington, D.C. 20535.

^{86}Sr , ^{91}Zr , ^{137}Ba , ^{142}Ce , and ^{207}Pb . The solutions were evaporated to near dryness to remove residual hydrogen fluoride. They were then transferred to quartz crucibles. After further evaporation, 5 mg graphite powder was added to each crucible to form a slurry. The slurry was evaporated to dryness on the hot plate, then the crucibles were transferred to a muffle furnace and heated for 15 to 30 min at 500°C. The purpose of the last step is to remove all volatile contaminants such as traces of acid or organic matter which might give mass spectral interferences.

The graphite powder was then compacted into electrodes and sparked in the usual manner. The line densities on the photoplate were read with a Joyce-Loebl Autodensitater and converted to ion intensities via the Hull transformation [4, pp. 194–203]. The measured altered isotope intensities were inserted into the following equation to calculate elemental concentrations [4, pp. 283–291].

$$X = [WK(A_{\text{sp}} - B_{\text{sp}}R)]/[M(BR - A)] \quad (1)$$

where

- X = elemental concentration in weight ppm, $\mu\text{g/g}$;
- W = weight of the isotopically enriched material added, μg ;
- M = weight of the sample, g;
- A = natural abundance of Isotope a;
- B = natural abundance of Isotope b;
- A_{sp} = abundance of Isotope a in the spike;
- B_{sp} = abundance of Isotope b in the spike;
- R = measured altered ratio of Isotope a to Isotope b; and
- K = ratio of the natural atomic weight of the element to the atomic weight of the spike.

Results and Discussion

Precision

Several of the samples were analyzed in triplicate to determine the precision of the technique. These results are shown in Table 1. The average relative standard deviation is 6.3%, excluding lead. This level of imprecision is mostly attributable to the errors involved in measuring isotopic ratios on the photographic plate. Careful measurement of isotopic ratios by an electrometer instead of a photoplate shows that the method is capable of 1% precision or better. This is illustrated in Table 2 for the major elements calcium and magnesium. (These elements were not determined for all the samples in this study since they are not expected to show much variation in window glass and a survey of several samples proved this to be true.) Electrometric measurements of isotope ratios of the trace elements are too time-consuming with the present instrumentation. The photoplate is therefore preferred for routine analysis, even though it will limit the precision to about 5%.

Accuracy

Since the primary justification of the ID-SSMS method is the absolute accuracy obtained, three National Bureau of Standards glass standards were analyzed by the same experimental technique as used on the window glass samples. The results are shown in Table 3. The agreement for SRM #612 is excellent except for iron. However, iron is satisfactorily determined for SRM #81 and #93, where the iron concentrations are

TABLE 1—Precision of analysis using photoplate detection. Mean concentrations \bar{X} and standard deviations σ are in ppm (triplicate runs).

Element	Sample 9	Sample 10	Sample 11	Sample 2733-1	Sample 2733-2	Sample 63841	Sample 642558	Avg RSD ^a
Potassium, \bar{X}	139	147	174	4790	3720	1510	1040	...
Potassium, σ	14	14	6	270	330	10	2	0.055
Iron, \bar{X}	740	890	800	870	860	660	510	...
Iron, σ	90	100	40	42	71	76	60	0.093
Rubidium, \bar{X}	42.7	30.5
Rubidium, σ	1.6	2.0	0.052
Strontium, \bar{X}	57.0	48.7	65.0	27.2	33.2	68.5	64.3	...
Strontium, σ	1.0	3.5	6.0	1.9	0.6	5.0	11	0.073
Zirconium, \bar{X}	73.0	61.0	74.0	29.1	11.8	45.2	52.3	...
Zirconium, σ	1.0	1.0	1.0	1.2	1.1	1.6	3.8	0.041
Barium, \bar{X}	12.7	13.6	15.2	21.4	22.8	35.5	36.6	...
Barium, σ	1.5	1.8	0.9	0.2	1.0	3.5	0.6	0.068
Cerium, \bar{X}	4.4	4.1	5.1	4.6	...
Cerium, σ	0.5	0.1	0.0	0.5	0.062
Lead, \bar{X}	7.2	9.4	11.4	6.5	...
Lead, σ	1.1	0.1	1.5	2.1	0.155

^a Relative standard deviation.

TABLE 2—Precision of analysis using electrometric detection. Mean concentrations \bar{X} and standard deviations σ in percentage by weight.

Element	Sample 9	Sample 10	Sample 11	Avg RSD ^a
Magnesium, \bar{X}	2.85	2.81	2.78	...
Magnesium, σ	0.02	0.02	0.02	0.007
Calcium, \bar{X}	6.25	6.14	6.07	...
Calcium, σ	0.06	0.07	0.20	0.015

^aRelative standard deviation.

closer to the values present in window glass. The only other discrepancy is the zirconium in SRM #93, for which there is no obvious explanation in view of the excellent agreement found for zirconium in SRM #81.

Homogeneity

Two different window panes, approximately 12 in. (305 mm) square, were sampled at extreme locations over the panes to determine the homogeneity of each element. The results in Table 4 show potassium, strontium, zirconium, and barium to be distributed uniformly over the window panes, since the relative standard deviation for these elements is comparable to the precision of measurement in Table 1. Iron, cerium, and lead appear to be measurably nonuniform. Rubidium was not at a measurable level in either pane, but its homogeneity should correspond to that of potassium in view of their chemical similarity.

Comparisons

The analyses of the FBI and Orange County window glasses are presented in Tables 5 and 6, respectively. In both tables, the samples have been arranged in order of decreasing potassium concentrations to facilitate comparisons. Most of the samples can be differentiated by inspection; however, it is obvious that a statistical comparison is required to make a decision on all the glasses. The statistical method we will use is that developed by Parker for comparison of evidence by multielemental analysis [5]. He defines a discrepancy index *C* for comparison of two samples in which *N* elements are measured:

$$C = \sum D_i^2 \tag{2}$$

where *D_i* is the reduced difference, that is, the difference in measured concentrations of Element *i* between the two samples *X_i* and *Y_i*, divided by the combined standard deviations.

$$D_i = (X_i - Y_i) / \sigma \tag{3}$$

The standard deviation σ is a combination of the precision of measurement θ and the intrinsic variation of the element within the sample ϕ .

$$\sigma^2 = \phi^2 + \theta^2 \tag{4}$$

If the two samples are identical, *D_i* will be distributed normally around the expectation value of unity, and *C* will be equivalent to chi-square with *n* degrees of freedom.

$$C \equiv \chi^2 \tag{5}$$

TABLE 3—Analysis of National Bureau of Standards glass standards (concentration in ppm).

SRM #	Potassium	Iron	Rubidium	Strontium	Zirconium	Barium	Cerium	Lead
612, determined	66	88	31.7	76.3	...	41.5	41.2	39.5
612, certified	64	51	31.4	78.4	...	41	39	38.6
81, determined	...	503	223
81, certified	...	512	230
93, determined	1120	490	70
93, certified	1300	530	96

TABLE 4—Homogeneity of window panes (concentrations in ppm).

Sample	Potassium	Iron	Strontium	Zirconium	Barium	Cerium	Lead
1 A	2630	700	45.0	47.5	30.2	3.8	5.8
1 B	2350	690	47.0	48.1	31.4	3.7	11.7
1 C	2500	700	39.0	45.0	30.1	3.9	8.9
1 D	2630	700	44.5	46.5	28.6	4.2	5.2
1 E	2570	740	42.5	47.9	31.6	4.1	5.5
Mean	2540	703	43.6	47.0	30.4	3.9	7.4
SD	120	22	3.0	1.3	1.2	0.2	2.8
2 A	3260	770	240	45.8	367	2.7	16.3
2 B	3430	610	248	46.9	408	4.8	10.7
2 C	3570	790	203	43.4	371	3.9	13.1
2 D	3500	420	236	44.3	391	2.8	17.9
Mean	3440	645	232	45.1	384	3.6	14.5
SD	130	174	20	1.6	19	1.0	3.2
Avg RSD ^a	0.043	0.15	0.078	0.032	0.045	0.16	0.30

^aRelative standard deviation.

TABLE 5—Analyses of FBI window glasses.

Sample	Refractive Index	Density	Concentrations in ppm						
			Potassium	Iron	Strontium	Zirconium	Barium	Cerium	Lead
8	1.5184	2.5046	1270	920	77	150	52	4.5	4.5
7	1.5184	2.5040	1100	1060	84	175	53	4.0	5.0
13	1.5185	2.5040	219	680	38	57	12.4	1.5	4.1
6	1.5184	2.5058	180	700	128	87	20	2.6	3.7
11	1.5186	2.5057	174	800	65	74	15.2	3.0	...
10	1.5186	2.5055	147	890	49	61	13.6	2.6	...
9	1.5186	2.5052	139	740	57	73	12.7	2.7	...
5	1.5183	2.5046	118	920	39	162	4.5	2.6	3.3

TABLE 6—Analyses of Orange County window glasses; refractive indices = 1.5165 ± 0.0002 (concentrations in ppm).

Sample	Potassium	Iron	Rubidium	Strontium	Zirconium	Barium	Cerium	Lead
63-463	6710	790	51.7	27.3	35.4	17.9	5.9	17.3
642557	5950	540	24.1	43.9	98.0	109	6.4	17.3
4608	5850	770	44.9	34.2	27.7	44.5	3.5	10.8
2763	5280	770	46.2	65.0	16.7	22.4	3.1	8.8
14504	5040	670	33.1	37.4	36.3	19.2	4.5	8.7
2733	4790	870	42.7	27.2	29.1	21.4	4.4	7.2
3910	4720	730	41.5	50.0	21.5	21.1	15.3	12.1
4008	4130	730	46.9	35.2	35.9	24.1	9.9	6.4
2773	3720	860	30.5	33.2	11.8	22.8	4.1	9.4
11043	3380	820	28.5	40.4	22.3	21.9	4.0	8.9
4084	1550	780	<10	71.0	45.5	38.5	5.0	4.8
63841	1510	660	<10	68.5	45.2	35.5	5.1	11.4
642682	1440	690	<10	68.7	50.0	36.9	5.2	8.5
4147	1370	630	<10	65.0	51.6	34.9	4.8	9.5
3962	1300	1000	<10	47.3	52.4	30.0	17.8	7.2
11257	1220	1360	<10	163	85.4	68.1	4.1	8.1
3993	1120	650	<10	105	96.6	69.1	9.2	6.4
642558	1040	510	<10	64.3	52.3	36.6	4.6	6.5
4758	1030	630	<10	71.0	42.9	41.5	2.4	11.5
66410	630	1120	<10	31.0	58.0	41.0	3.6	6.7

The value for σ was considered to be equal to the precision standard deviation in Table 1 for the elements potassium, strontium, rubidium, zirconium, and barium, which have negligible inhomogeneity. For the inhomogeneous elements iron, cerium, and lead, σ was considered to be equal to the relative standard deviations shown in Table 4, since it reflects both θ and ϕ .

Before applying Eq 2, we wish to determine which of the elements are the most useful for distinguishing glasses of similar physical properties. This may be done by computing the average reduced differences from Eq 3 for all pairs of glasses in Table 5 and Table 6, respectively. If the average D for a given element is not much greater than unity, it will generally be useless for differentiating purposes and should not be included in the statistical comparisons because it will only add "noise" to the data. The average reduced differences are shown in Table 7. Potassium, rubidium, strontium, zirconium, and barium appear to be the most useful elements for differentiation. Iron and lead are of no use whatsoever, and cerium is only a little better. We will therefore compute the discrepancy index C using only the former elements.

The statistical comparisons are shown in Table 8. For the sake of brevity, only those pairs are shown which are reasonably similar. The probability of the computed C value is taken from the tables of chi-square. This is the probability of the measurements having that much discrepancy, or more, assuming the pair of samples are from the same source, or window pane. A confidence level must be established by the investigator, at which samples will be excluded from being identical. Conventionally, this is set at 99 or 95%, corresponding to probabilities of 0.01 or 0.05, respectively. In other words, if the prob-

TABLE 7—Average reduced differences for the elements.

Element	\bar{D} , FBI	\bar{D} , Orange County
Potassium	8.5	8.4
Iron	0.9	1.2
Rubidium	...	4.0
Strontium	4.3	4.6
Zirconium	8.2	9.2
Barium	7.1	4.8
Cerium	1.5	2.0
Lead	0.5	0.8

TABLE 8—Statistical comparisons of glass samples.

FBI Samples			Orange County Samples		
Pair	C	Probability	Pair	C	Probability
7, 8	11.1	0.03	4084, 63841	1.0	0.90
9, 10	12.6	0.02	4147, 642682	1.3	0.85
9, 11	13.3	0.01	63841, 642682	3.6	0.47
10, 11	24.2	<<0.01	4084, 642682	3.8	0.45
10, 13	32.8	<<0.01	4147, 63841	7.0	0.13
All others	33	<<0.01	4147, 4084	8.9	0.06
			4147, 3962	12.1	0.02
			4147, 642558	12.5	0.02
			4758, 642558	14.1	0.01
			642682, 642558	17.8	<0.01
			3962, 642682	19.3	<0.01
			All others	>20	<<0.01

ability is 0.01 or less, we are at least 99% confident that the samples did not come from the same window pane.

At the 95% confidence level, all of the FBI glasses are distinguished. However, the Orange County glasses 4084, 4147, 63841, and 642682 are not distinguishable from one another at this level, and in fact match each other quite well. At the more rigorous 99% confidence level, there are three pairs of FBI glasses and two additional pairs of Orange County glasses that cannot be distinguished. In summary, of 28 pairs of FBI glass comparisons, all are distinguishable at the confidence level of 95% and 25 are distinguishable at the confidence level of 99%. Of 190 pairs of Orange County glasses, 184 are distinguishable at the 95% confidence level and 182 are distinguishable at the 99% confidence level.

Conclusions

The elements potassium, rubidium, strontium, zirconium, and barium can be determined with a precision and accuracy of about 6%. They appear to be homogeneously distributed within window panes to at least this level of precision. Like other elemental analysis techniques, ID-SSMS is able to distinguish most glasses having similar physical properties.

The advantage of ID-SSMS is its ability to determine absolute concentration, facilitating the accumulation of a data base. The main disadvantage is the time required for analysis. Using the present procedures, approximately three man-days are required for analysis of six samples. It is obvious that measurements of refractive index or density, or both, must be used to screen samples prior to analysis by ID-SSMS. Only those found to be indistinguishable by physical properties should be subjected to elemental analysis.

Summary

Elemental analysis by the method of isotope dilution spark source mass spectrometry has been applied to the comparison of window glasses having similar physical properties. The method is both accurate and precise, with a relative standard deviation of approximately 6%. Potassium, rubidium, strontium, zirconium, and barium are found to be useful elements for characterizing window panes. Iron, lead, and cerium are of little use because of their inhomogeneity within the panes. In one set of glasses, 25 of 28 possible comparisons are found to be distinguishable at the 99% confidence level. In the other set, 182 of 190 possible comparisons are found to be distinguishable.

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Scientific and Technical Services Division
Federal Bureau of Investigation
Washington, D.C. 20535