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CASE REPORT

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Elemental Analysis of Glass Fragments by ICP-MS as Evidence of Association: Analysis of a Case

ABSTRACT: Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze glass evidence from a case in which a person broke a window in each of 15 vehicles in a parking lot in order to gain entry into the vehicles. The results of the analysis by traditional methods, which measure the properties of color, thickness, density, and refractive index, are also reported. A total of 15 known samples representing the windows on the cars and 42 questioned glass fragments recovered from the suspect and the police vehicle where the suspect was sitting were submitted for analysis. Density comparisons separated one of the known samples into three samples, increasing the number of known samples from 15 to 17. The concentrations of 16 elements were measured for all but three of the samples using an external calibration ICP-MS method with internal standardization. Color assessment (non-instrumental) separated the 17 known samples into two groups, and refractive index measurements resulted in six groups when the Emmons double variation method was used and ten groups when the Glass Refractive Index Measurement 2 (GRIM2) system was used. Elemental analysis, by itself, differentiated all of the known samples from each other and associated four of the known sample fragments with several of the questioned sample fragments. The informing power of RI, density, and elemental analysis comparisons is evaluated and a summary of the case results is reported.

KEYWORDS: forensic science, glass comparisons, elemental analysis, refractive index, inductively coupled plasma mass spectrometry

Glass fragments are frequently encountered as evidence in hit-and-run, burglary, and other types of crime scenes. Previous studies and reports (1–3) have improved the understanding of the variation of the physical, optical, and chemical properties of glass within a single source and between sources of a population. The properties of color, thickness, density, refractive index, and elemental composition can be used to include glass fragments into a group (4–6) (as is used in classification schemes) as well as to characterize the glass to associate a fragment recovered from a crime scene with another fragment from a known source. One approach to associate glass fragments is to compare the fragments on the basis of their physical, optical, and chemical properties. Having found the glass sample fragments to be indistinguishable, an examiner may state the informing power of the test and draw conclusions regarding the value of the association. The use of a sensitive test (or tests) translates to a more significant association between the fragments. Some tests such as color, thickness, and density comparisons are of value for relatively large fragments, but that is not the usual situation regarding fragments recovered in transfer evidence cases. The more frequently encountered glass sample is of a size more amenable for refractive index and, sometimes, elemental composition determinations.

Glass manufacturing is a very sophisticated industry that devotes considerable resources to reduce the variation of some of the very same physical and optical properties upon which forensic scientists depend on to differentiate between glass fragments. Industry and manufacturing standards, for instance, are tailored to produce glass with a consistent refractive index over a long period of time (2,4), as evidenced by recent reports of small overall ranges for RI in glass manufacturing (7). Many workers have reported the utility of elemental composition comparisons as a tool for improved discrimination between glass fragments (8–10). The measurement and comparisons of the trace level ($\sim\mu g/g$ range) elements in the bulk glass have been shown to provide a particularly good manner of discrimination between glass fragments (11–13). Furthermore, ICP-MS has been demonstrated (14–16) to be an excellent technique for the determination of the trace elemental content in glass. This technique combines the capability of multi-elemental analysis with a high degree of sensitivity, allowing fast elemental analysis of small size ($\sim$2 mg) glass samples. The following case demonstrates the power of discrimination of ICP-MS as an analytical method for glass analysis and the improvement in informing power of elemental analysis by this method over other measured properties such as color, thickness, density, and refractive index.

Case Summary

A person broke a window in each of 15 vehicles that were parked in an airport's parking lot in order to gain entry to the vehicles. Nearby, a suspect was stopped by police and apprehended

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after trying to run away. The overalls he was wearing were searched and 28 glass fragments were recovered from the pockets and surfaces of the overalls. Fourteen additional glass fragments were found in the police vehicle in which the suspect was transported while in custody. These fragments were collected because it was thought that they were present as a result of a secondary transfer from the suspect to the police vehicle. Charlotte-Mecklenburg Police Department (CMPD) crime scene technicians retrieved samples of glass from the broken windows on all 15 vehicles. The 15 known samples corresponded to 13 side windows, one wing window, and one sliding window from a pick-up truck. The known samples and the recovered fragments were submitted to the CMPD forensic laboratory for analysis. The known samples were visually inspected and their densities were compared using a variation of a previously published ASTM method for density comparisons (17–19). This first examination was conducted to verify that the known fragments were uniform, to identify potential contamination, and to determine if some of the recovered fragments could be grouped together by physical features. Fragments from one of the known samples produced three distinct groups based on density differences within the fragments, thereby increasing the number of known exhibits from 15 to 17. The CMPD laboratory also conducted thickness and refractive index measurements of the known and recovered fragments (when possible) using the Emmons double variation method for refractive index measurements (20) (see Tables 1 through 4 for a summary of the results). The 17 known samples and the questioned (recovered) samples were submitted to the

TABLE 1—*Source and thickness ranges of the known samples.*

Sample	Thickness (in inches)	Vehicle Source
K1	0.1610–0.1615	1999 Chevrolet Tahoe
K2	0.1515–0.1520	2001 Ford Van
K3	0.2231–0.2240	1993 Chevrolet Beauville
K4	0.1510–0.1516	1999 Ford Explorer
K5	0.1628–0.1634	1996 Jeep Cherokee
K6	0.1508–0.1518	1989 Ford Econoline Van
K7	0.1395–0.1401	1998 Jeep Wrangler
K8	0.1604–0.1610	1999 Chevrolet Tahoe
K9	0.1354–0.1360	1998 Ford Ranger
K10	0.1878–0.1881	1988 Oldsmobile Touring Sedan
K11	0.1916–0.1926	1998 Cadillac STS
K12	0.1915–0.1924	1997 Cadillac STS
K13	0.1526–0.1530	1993 GMC Sierra
K14	0.1279–0.1285	1994 Ford Ranger
K15	0.1628–0.1640	2000 Dodge Dakota

TABLE 2—*Summary of thickness comparisons for the known samples.*

Group	Samples
1	K14
2	K9
3	K7
4	K6, K4, K2
5	K13
6	K8, K1
7	K5, K15
8	K10
9	K12, K11
10	K3

TABLE 3—*Groups obtained by comparison of densities of the known samples. The groups are presented in increasing density (no numerical values were determined for individual density measurements).*

Group	Sample
1	K5, K10
2	K3
3	K6, K7
4	K15
5	K14
6	K2
7	K12, K13
8	K11
9	K1
10	K9
11	K8a
12	K4
13	K8b
14	K8c

TABLE 4—*Summary of refractive index comparisons for the known samples using the Emmons double variation method (fixed match criteria of ± 0.0002 RI units) and GRIM 2 method (t-test, $p < 0.05$). Groups are presented in increasing RI values.*

Group	Samples Grouped by the Emmons Double Variation Results at CMPD (fixed criteria ± 0.0002 RI units)	Samples Grouped by the GRIM2 Results at IFRI (t-test $p < 0.05$)
1	K10, K7, K5, K6, K3	K10, K5, K7
2	K7, K5, K6, K3, K15	K7, K3
3	K14	K15, K6
4	K2, K13, K1	K14
5	K11, K12	K2, K13
6	K9, K8a, K8c, K8b, K4	K1
7		K12
8		K11
9		K9, K8a, K4
10		K4, K8c, K8b

International Forensic Research Institute (IFRI) laboratory for further analysis.

Materials and Methods

Thickness

Thickness measurements were conducted only on fragments exhibiting a full-pane width by the CMPD laboratory. The thicknesses of several fragments within each sample were measured using a Dial-Cal 599-579-4 caliper (Brown & Sharpe Mfg. Co., Switzerland). This property was not measured at the IFRI laboratory.

Density

The density comparisons were conducted at the CMPD Laboratory based on previously published methods (17–19). Particles were cleaned using an ultrasonic bath (Ultrasonics, Inc., Plainview, NY) and the fragment shapes were recorded for identification. The cleaned particles were then placed into a glass tube filled to a fixed volume with a mixture of bromoform (Fluka, Buchs, Switzerland) and bromobenzene (Sigma-Aldrich Corp., St. Louis, MO). The density of the starting solution is verified to be between 2.485 and 2.515 g/mL using sink float standards (Cargille Laboratories, Inc., Cedar Grove, NJ). The tube was placed in a water jacket to dampen any convection current movement. The density of the solution was adjusted using a known volume of one of the solvents to change the density of the solution by 0.001 g/mL. The particles were observed to sink, float, or remain suspended relative to the other particles. Although no numerical values were obtained for the density measurements, the comparisons were used as a means to distinguish between different fragments.

Refractive Index

The standard test method described in ASTM 1967–98 (21) was used for the determination of the refractive index measurements at 589 nm at the IFRI laboratory. Immersion oil B from Locke Scientific (Hants, UK) was calibrated with B2, B3, B4, B6, and B10 reference glasses (Locke Scientific, Hants, UK) and checked with PK3 (Schott, Duryea, PA). The refractive index measurement system used was a GRIM2 (Foster and Freeman, Worcestershire, UK) equipped with a FP82 hot stage (Mettler, Grifensee, Switzerland). Each reported refractive index value was the result of the mean of the measurements from five sample portions of a given fragment.

A variation of the standard test method described in AOAC 973.65 (20) was used for the determination of the refractive index measurements in the CMPD laboratory. Calibrated immersion liquid 710R fluid (Dow Corning, Midland, MI) was used to find the matching temperatures and wavelengths and checked with a standard glass Cargille II (Cargille Laboratories, Inc. Cedar Grove, NJ). The refractive index measurement system used was an Olympus BX60 (Olympus Optical Co., LTD, Tokyo, Japan) equipped with a LTS350 hot stage, a TMS93 controller, and LikSys software (Linkam, Surrey, England). Refractive index values were calculated for several match points. Each match point was the result of the mean of several measurements of a fragment. The match points were then plotted on Hartmann net graph paper on which the dispersion curve had previously been plotted for the 710R fluid. The refractive index values were then recorded for 656, 589, and 486 nm, which were then used for comparative purposes, extrapolating to obtain values for 486 and 656 nm when necessary.

ICP-MS External Calibration with Internal Standardization

High-purity water ($>$18 MΩ-cm) was obtained with a Nanopure Infinity purification system (Barnstead, Dubuque, IA). Trace metal grade (Optima grade) nitric (HNO_3), hydrofluoric (HF) and hydrochloric acids (HCl) (Fisher, Pittsburgh, PA) were used throughout the analysis. Two optical glass standard reference materials (SRMs), NIST 612 and NIST 1831, were analyzed with each sample set to check for any day-to-day variation. Multi-element standards were prepared with single element 1000 mg/L stock solutions (GFS Chemicals, Columbus, OH). The calibration verification standard solutions were prepared with single element standard 1000 mg/L stock solutions purchased from another vendor (Spex-Certiprep, Metuchen, NJ). Two calibration curves, used to measure trace and minor element concentrations as well as to check standards, were prepared by diluting the stock solutions to working solutions using 0.8 mol/L HNO_3. For the purposes of this work, the trace elements were defined as being present in concentrations of less than 1000 μg/g in the glass, and the minor elements were defined as being present in concentrations greater than 1000 μg/g in the glass. For the first calibration curve, six different concentration standards were prepared with rhodium (Rh) as the internal standard (final concentration of 50.0 μg/L), and the elements were grouped according to the expected concentrations in the glass. The first group, consisting of magnesium (Mg), titanium (Ti), manganese (Mn), strontium (Sr), zirconium (Zr), antimony (Sb), barium (Ba), and lead (Pb) was prepared in concentrations ranging from 0 to 100 μg/L. The second group comprised of gallium (Ga), rubidium (Rb), lanthanum (La), cerium (Ce), samarium (Sm), and hafnium (Hf) were prepared in concentrations ranging from 0 to 10 μg/L. The check standard for the first curve was 50.00 μg/L for each of the elements of the first group and 5.000 μg/L for the elements of the second group. The second calibration curve included scandium (Sc) as the internal standard (final concentration 60.0 μg/L) and was composed of four standards of magnesium (Mg), aluminum (Al), and iron (Fe) prepared in concentrations ranging from 0 to 150 μg/L. The check standard for this curve has a final concentration of 60 μg/L in all elements.

The samples were washed, first in methanol for 10 min, then with 1.6 mol/L HNO_3 for 30 min and rinsed with high-purity water. After rinsing, they were left to dry overnight. The glass was sampled, crushed, and weighed in triplicate (approximately 2 mg $\pm$ 1 μg) into 5.000 mL polypropylene test tubes (Falcon, Franklin Lakes, NJ). The glass samples were digested by adding a 600 μL solution of a digestive mixture containing HF, HCl, HNO_3 (2:1:1) to each test tube before capping them. After 120 min inside an ultrasonic bath, the tubes were uncapped and set into a dry bath heating block (80 $\pm$ 5°C) until the samples were completely dry (24 to 36 h). The samples were reconstituted using 0.8 mL of 4 mol/L HNO_3, 20 μL of 10 μg/L Rh in 0.8 mol/L HNO_3, and 0.680 mL of deionized water and then left overnight. An additional volume of 2.500 mL of deionized water was added and the samples vigorously mixed. Prior to measuring these solutions, an aliquot of 50 μL from each sample was diluted by transferring it to an 8 mL test tube (Falcon, NY) and mixing it with 30 μL of 10 μg/L Sc in 0.8 mol/L HNO_3 and 4.920 mL of 0.8 mol/L HNO_3. The undiluted samples were measured using the first calibration curve, and the 1:100 dilutions were measured using the second calibration curve.

The ICP-MS system used for this work was an Agilent (HP) 4500 Plus Shield Torch System (Agilent, Palo Alto, CA) equipped with an autosampler ASX-500 (CETAC, Omaha, NE), a nebulization system composed of a peristaltic pump, a Babington nebulizer, and a Scott-double pass spray chamber kept at 14°C.

The plasma experimental parameters used are described below.

RF Power	1162 W
RF Matching	1.95 V
Carrier gas (argon)	1.06 L/min
Blend gas	None
Plasma gas (argon)	16.6 L/min

Statistical Analysis of the Data

A personal computer equipped with SYSTAT for windows (SPSS Corp., v6.1) and Excel (Microsoft Corp., v9.0.2719) was used for the statistical analysis of the data. The pairwise comparisons (multiple comparisons) were carried out using analysis of variance (ANOVA). However, the results of an ANOVA table serve only to indicate whether these multiple means differ significantly (22) without identifying which of the means were significantly different. For that purpose, the Tukey's post hoc test was selected to determine which pairs of means differed significantly ($p < 0.05$). This post hoc test uses the studentized range statistic to make all pairwise comparisons between groups, and it is a powerful post hoc test for a large number of pair comparisons. A t-test not assuming equal variances was used whenever a single pair comparison was made.

Results and Discussion

Thickness measurements conducted at the CMPD forensic laboratory of the known samples resulted in ten distinct groups (see Tables 1 and 2). Two samples were considered in the same group if there was an overlapping of ranges. The CMPD forensic laboratory found that fragments from one of the known samples (K8) produced three density groups (K8a, K8b, K8c), therefore increasing the number of known samples from 15 to 17. The density comparisons of the 17 known fragments produced 14 groups as shown in Table 3. Refractive index measurements conducted at the CMPD forensic laboratory of the known samples using the Emmons double variation method resulted in six groups (see Table 4). The samples were considered in the same group if there was an overlap within ±0.0002 RI units. The groups were found to be not exclusive: for example, K3 matches K10 and K15 using the mentioned criteria, but K10 and K15 do not match. The IFRI laboratory received the 17 known samples and the 15 questioned samples. A color assessment (non-instrumental) was performed, separating the 17 known fragments into two groups. Refractive index measurements of the known samples using the GRIM2 resulted in ten groups using a t-test ($p < 0.05$) for matching criteria (see Table 4). The groups were not exclusive. Elemental analysis performed at the IFRI laboratory differentiated all the known samples from each other. A typical dataset for the comparison of K3 and K7 is shown in Table 5. Therefore, for $p < 0.05$, K3 and K7 are distinguishable from each other (significantly different) by the concentrations of Mg, Ti, Mn, Fe, Sr, Zr, Ba, La, Ce, Sm, Hf, and Pb. All 17 known samples were compared to each other, generating a total of 136 possible comparisons. Analysis of the results from 136 possible comparison pairs using the statistical tests described above results in 12 indistinguishable pairs by refractive index, and all of the comparison pairs are distinguishable when elemental analysis is used.

TABLE 5—*Typical dataset of a comparison between two fragments known to have originated from different sources (K3 and K7). Elemental concentrations are reported in $\mu g/g$ for three separate digestions from the crushed sample and three aspirations for each digestion. Elements found to be significantly different are shown in bold (all except Ga and Rb are significantly different at $p < 0.05$).*

Parameter		Sample	
		K3	K7
Refractive Index	average	1.51870	1.51869
	SD	0.00011	0.00009
Mg	average	16072	21307
	SD	1698	2639
	% RSD	10.6	12.4
Ti	average	114.8	61.57
	SD	2.1	2.09
	% RSD	1.8	3.4
Mn	average	16.9	20.39
	SD	0.48	0.76
	% RSD	2.8	3.7
Fe	average	2951	3719
	SD	170	115
	% RSD	5.8	3.1
Ga	average	0.092	0.11
	SD	0.026	0.006
	% RSD	28.3	5.5
Rb	average	0.679	0.707
	SD	0.01	0.087
	% RSD	1.5	12.3
Sr	average	76.86	22.99
	SD	0.52	0.52
	% RSD	0.7	2.3
Zr	average	127.2	79.68
	SD	2.65	1.41
	% RSD	2.1	1.8
Ba	average	9.95	5.998
	SD	0.288	0.794
	% RSD	2.9	13.2
La	average	1.456	1.921
	SD	0.034	0.035
	% RSD	2.3	1.8
Ce	average	2.372	3.507
	SD	0.094	0.13
	% RSD	4.0	3.7
Sm	average	0.163	0.262
	SD	0.022	0.03
	% RSD	13.5	11.5
Hf	average	3.112	1.867
	SD	0.189	0.057
	% RSD	6.1	3.1
Pb	average	1.459	1.215
	SD	0.036	0.022
	% RSD	2.5	1.8

A typical dataset for the comparison between a recovered fragment and a known fragment (when the pair is found to be indistinguishable) is summarized in Table 6. Using the results from elemental analysis performed by IFRI, the recovered (questioned) samples were determined to belong to one of five possible distinct groups (Table 7), and four these groups were related to individual known vehicles. The refractive index measurements by the GRIM2 did not add information for the discrimination of these samples, and due to the nature and size (these fragments were not full pane width), it was not possible to measure thickness for the samples received by the IFRI laboratory. The results of the analysis performed at the CMPD laboratory using a combination of thickness, color, density, and refractive index by the Emmons double variation method are also presented in Table 7.

The measurements taken at CMPD were able to distinguish all the known samples into 17 distinct groups using the classical comparison techniques of thickness, RI, and density. Of the measurements and comparisons conducted in the CMPD laboratory (and not including the elemental composition analysis conducted at

TABLE 6—*Comparison of RI and elemental composition for known sample K2 and recovered samples Qb and Qc (all comparisons are indistinguishable by t-test $p < 0.05$). Elemental concentrations are reported in μg/g for three separate digestions from the crushed sample and three aspirations for each digestion.*

Parameter		Sample		
		K2	Qb	Qc
Refractive Index	Average	1.52015	1.52008	1.52012
	SD	0.00007	0.00012	0.00013
Mg	Average	17461	20497	20163
	SD	1207	1472	798
	% RSD	6.9	7.2	4.0
Al	Average	2391	2596	3042
	SD	268	246	322
	% RSD	11.2	9.5	10.6
Ti	Average	71.22	68.91	70.33
	SD	1.52	3.49	2.46
	% RSD	2.1	5.1	3.5
Mn	Average	44.22	44.49	43.55
	SD	0.97	1.54	1.53
	% RSD	2.2	3.5	3.5
Fe	Average	5694	5477	5775
	SD	391	201	216
	% RSD	6.9	3.7	3.7
Ga	Average	0.473	0.559	0.57
	SD	0.035	0.08	0.03
	% RSD	7.4	14.3	5.3
Rb	Average	1.946	1.934	1.943
	SD	0.059	0.1	0.041
	% RSD	3.0	5.2	2.1
Sr	Average	21.8	21.65	21.85
	SD	0.36	1.02	0.28
	% RSD	1.7	4.7	1.3
Zr	Average	24.93	24.64	24.72
	SD	0.14	1.22	0.21
	% RSD	0.6	5.0	0.8
Ba	Average	1.72	2.168	2.189
	SD	0.312	0.305	0.054
	% RSD	18.1	14.1	2.5
La	Average	2.69	2.642	2.699
	SD	0.005	0.134	0.023
	% RSD	0.2	5.1	0.9
Ce	Average	5.247	5.199	5.173
	SD	0.095	0.316	0.209
	% RSD	1.8	6.1	4.0
Sm	Average	0.276	0.258	0.263
	SD	0.033	0.04	0.022
	% RSD	12.0	15.5	8.4
Hf	Average	0.602	0.518	0.560
	SD	0.038	0.024	0.037
	% RSD	6.3	4.6	6.6
Pb	Average	0.779	0.847	0.760
	SD	0.301	0.035	0.138
	% RSD	38.6	4.1	18.2

TABLE 7—*Summary results of the comparisons by elemental composition and by classical methods (density, thickness, color, and refractive index with Emmons double variation).*

Groups Associated by Elemental Composition*	Groups Associated by Classical Methods[†,‡,§]
K2, Qb, Qc	K2, Qb
K5, Qn	K5, Qn
K7, Qh, Qi, Qm	K7, Qi
K15, Qa, Qk	K15, Qa
Qd and Qg and Qj	K4, Qd
	K6, K7, Qo
	K13 and Qc

[*] Qe, Qf, and Qo were too small for elemental analysis. However, their refractive index measurements by the GRIM2-grouped Qe and Qf with K4, K8b, K8c, Qd, Qg, and Qj; and Qo with K3, K7, Qh, Qi, Ql, Qm, and Qn.

[†] Due to the size of Qb, Qc, Qd, Qe, Qf, and Qo, it was not possible to measure their thickness. Therefore, some consistencies between these samples only take into account the density and RI values.

[‡] Refractive index measurements were not performed in Qe, Qf, Qh, Qk, Ql, and Qm due to either differences expressed in previous examinations or a sample grouped by density with other particles for which an association was made.

[§] Qo was too small for a thickness measurement and is therefore considered consistent with both K6 and K7 even though known samples K6 and K7 are distinguishable from each other by thickness.

IFRI), density provides the best discrimination (separating all the known samples into 14 distinct groups). It is useful then to further examine the informing power of density when it is used by itself as means for discrimination between glass fragments. Although most of the known samples were separated by density, there were three examples (K5-K10, K6-K7, and K12-K13) in which density indicated an association for glass samples known to originate from different sources. There were ten additional associations of recovered fragments with known fragments found by density but that were not found by elemental comparisons, and three associations by elemental analysis that were not found by density (Table 8). It's important to note that density is a function of the glass chemistry and cooling history. It is possible that two specimens could have the same chemical composition and different cooling histories, resulting in different densities.

TABLE 8—*Comparison of the indistinguishable pairs obtained by elemental composition and density alone.*

Pairs Associated by Density and Not Associated by Elemental Composition	Pairs Associated by Elemental Composition and Not Asociated by Density
K3, Qh	K2 and Qc
K3, Ql	K7 and Qh
K4, Qd	Qb and Qc
K4, Qg	
K4, Qj	
K6, Qi	
K6, Qm	
K10, Qn	
K12, Qc	
K13, Qc	
K5, K10	
K6, K7	
K12, K13	

Conclusions

The combination of thickness, density, and refractive index comparisons enabled the initial screening of all the known fragments and produced 17 separate groups of glass fragments from the original 15 known samples submitted. A total of 136 comparison pairs are possible when comparing all 17 known samples to each other, and all of them were distinguished by elemental analysis by ICP-MS. The informing power of elemental analysis by a sensitive technique such as ICP-MS, used by itself, produces excellent evidence of association between glass fragments as shown by the differentiation of the known vehicle windows. The traditional methods (color, thickness, density, and refractive index) of forensic glass analysis when taken into account collectively were able to differentiate all of the known samples from each other. While density comparisons alone were reported to produce very good discrimination between the known samples, density comparisons produced three associations between fragments known to originate from different sources. There were 13 additional instances of disagreement between the density comparisons and the ICPMS data when comparing the known samples (Ks) to the recovered samples (Qs). ICP-MS is particularly useful for samples in which the thickness cannot be measured, as is the case with most recovered glass fragments. Straightforward statistical analyses of the data generated were used to both differentiate between fragments known to originate from different sources and to associate the recovered fragments to some of the known fragments.

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