

**PAPER****CRIMINALISTICS**

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## Comparison of Glass Fragments Using Particle-Induced X-Ray Emission (PIXE) Spectrometry\*,†

**ABSTRACT:** A procedure has been developed to analyze the trace element concentrations in glass fragments using particle-induced X-ray emission (PIXE) spectrometry. This method involves using accelerated protons to excite inner-shell electronic transitions of target atoms and recording the resultant X-rays to characterize the trace element concentrations. The protocol was able to identify those glass fragments that originated from different sources based on their elemental analyses. The protocol includes specific approaches to calculating uncertainties and handling measurements below the level of detection. The results indicate that this approach has increased sensitivity for several elements with higher atomic number compared with X-ray fluorescence methods. While not as sensitive as laser-ablation or inductively coupled plasma mass spectrometry methods of dissolved samples, it is entirely nondestructive and entails a much simpler sample preparation process that may be used to presort glass fragments for more comprehensive elemental analysis. As such, the technique described may have a niche role in forensic glass analysis.

**KEYWORDS:** forensic science, particle-induced X-ray emission, nondestructive, glass, trace elements, statistical tests

Characterization of glass fragments is a common activity in forensic science. Many analytical methods to analyze glass have been developed and are in routine use in laboratories around the world (1–10). Historically, the physical properties, such as the color and refractive index, have been sufficient in most cases to compare a particular glass fragment with a specific source. Some forensic scientists believe that improved manufacturing processes and increased quality control in the production of various glasses have reduced the variation of these properties so that additional techniques are required to successfully discriminate between various sources of modern glass. Even if the globalization of glass production results in more variation in the refractive index, additional nondestructive techniques would be useful if the samples under consideration have similar color and refractive index. Almost all of the techniques in use to characterize glass fragments beyond refractive index involve the quantitative analysis of trace elements in glass. Often, the different amounts of various trace elements in each glass fragment allow conclusions about the origin of recovered glass fragments. Common analytical methods used in forensic studies of glass include energy-dispersive X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), and laser-ablation inductively coupled plasma mass spectrometry

(LA-ICP-MS). XRF is by far the easiest and lowest-cost nondestructive elemental analysis technique for glass. However, it is typically the least sensitive of the three trace element techniques listed. Many fluorescence methods (such as SEM-EDS) only sample the top surface of the glass, typically less than a few microns, which can lead to reproducibility concerns, and they do not effectively excite the trace elements with higher atomic number that are present in most glass samples (11,12).

Cathodoluminescence spectroscopy has been investigated as a possible nondestructive technique, but is not yet well developed (13). All ICP methods are significantly more sensitive to trace elements found in glass; however, they are more costly and involve either the complete or partial destruction of the samples to be compared. For example, most ICP methods often involve the complete digestion of the glass fragments in hydrofluoric acid and subsequent replicate analysis of the elemental solutions. Laser ablation can avoid the complete destruction of the forensic sample, but surface-pitting by the laser during the ablation process does lead to additional uncertainties in the measured elemental concentrations because of the change in measurement parameters during the ablation process (3,4,8).

In an effort to find a better, nondestructive yet sensitive method to analyze the trace elemental concentrations within glass samples, a procedure has been developed to quantitatively compare glass fragment samples with particle-induced X-ray emission (PIXE) spectrometry. Because PIXE uses an accelerated ion beam to excite X-ray emission within the samples, it has higher production cross sections for X-rays from heavier trace elements within glass samples. In addition, the energetic ion beams can penetrate deeper into the glass, and the resultant higher-energy X-rays from heavier elements can escape from the samples' surface more readily, avoiding some of the concerns of surface analysis versus bulk volume

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analysis. The technique described here allows the determination of multiple trace elemental concentrations with associated uncertainties. If one or more of the nine measured trace elements are found to be significantly different, based on the particular uncertainties, the assumption is then that the fragments have different provenance. Like XRF, PIXE is nondestructive and while it does not have the sensitivity of the ICP methods, its value may lie in its ability to relatively rapidly discriminate between glass fragments that cannot be distinguished by XRF alone and still be nondestructive. Admittedly, the PIXE technique requires a significant capital investment in instrumentation, but for established ion beam analysis laboratories, this application of PIXE can provide a detailed quantitative characterization of glass fragments, while simultaneously leaving the samples unchanged.

An additional goal during the development of this method was to minimize the time needed for the testing. PIXE is a very sensitive technique but, like many techniques, requires significant time to achieve maximum levels of sensitivity. In this work, the measurement times were intentionally kept short (on the order of minutes), even though this reduces the overall sensitivity, to process samples quickly. This increases the difficulty in making comparisons and led to some *ad hoc* testing limits as described below.

## Methods

### PIXE Measurements

The basic thick-target PIXE technique involves directing a beam of energetic protons onto a solid sample such as glass where the measured X-rays induced in the sample give information about the composition of the sample (11,12). While the basic PIXE technique is straightforward, there are many experimental variables that can affect the results.

The energy of the protons was set to the machine maximum, 3.4 MeV for the Hope Ion-Beam Analysis Laboratory (HIBAL), to enhance the production of X-rays from the higher atomic-number elements. Higher beam energies also allow deeper penetration depths into the surface of the glass (*c.* 100  $\mu\text{m}$ ), which helps to reduce surface effects in the elemental characterization of the glass. The beam spot size for the measurements reported here was fairly large, *c.* 1.5 mm in diameter, which also helped to average over local variations in elemental concentration. Background bremsstrahlung radiation was not a problem because only elements with atomic numbers equal to Ca and higher (X-ray energies above 3.6 keV) were considered and because the beam intensity was kept below 5 nA. Because glass is electrically insulating, either the surface must be coated with a conductive material, or the beam current must be kept low to prevent background radiation. In keeping with the nondestructive nature of the testing, we opted for lower beam currents on target and slightly longer data acquisition times, rather than coating the samples with conductive materials. The absolute beam current is measured by moving the samples out of the beam path so that the beam can impact an aluminum Faraday cup and was measured before and after individual measurements with a Brookhaven Instruments Corporation model 1000C current integrator. Fluctuations in the beam current during data collection were also monitored by simultaneously measuring elastically scattered protons (Rutherford Backscattering) with a surface barrier detector positioned at 168.2°. From the run length and monitored beam intensity, the total amount of charge on target was calculated, typically 2–3  $\mu\text{C}$  per measurement. A thin mylar filter, *c.* 500  $\mu\text{m}$ , was placed between the sample and the X-ray detector to reduce the X-ray count rate because of silicon

(1.79 keV) and bremsstrahlung background count rate (peaked below 4 keV). While a thinner filter would have allowed elements with atomic number <20 to be detected more quantifiably, with this beam energy and a permanent Be detector window, the quantification would be marginal for Na, Mg, and Al because the correction factors for attenuation are unacceptably large. Thus, these important trace elements that typically occur in glass (14) were not included in this analysis. The count rate in the X-ray detector was always kept <1000 Hz, and the dead time was always less than 0.1% as a result.

Before the glass fragment samples were mounted for analysis, they were thoroughly cleaned first with methanol, and then immersed in trace-metal grade 1 M  $\text{HNO}_3$ . Finally, they were rinsed with deionized water and air dried in a covered container to minimize airborne contamination. During and after this cleaning process, latex gloves and laboratory cleaning tissues were used to handle the samples. Samples were mounted with the front surface normal to the beam by gently pushing them into a thin layer of Apiezon Q™ with a drill press. This minimized variations from self-absorption of X-rays emitted from within the sample which is very dependent on the orientation of the sample surface. No polishing is carried out on the surface of the glass, as this would defeat the nondestructive nature of the testing method.

The X-rays were detected in an Ortec Si(Li) detector (10 mm diameter by 5.35 mm thick, 165 keV nominal resolution, at a distance of 30 cm from the target) situated 135° from the particle beam direction with a *c.* 500  $\mu\text{m}$  mylar filter in front of the detector. A typical X-ray spectrum from a glass fragment with this thick filter is shown in Fig. 1. Each X-ray spectrum was analyzed for nine elements: Ca, Ti, Cr, Mn, Fe, Cu, Zn, Sr, and Zr. In many cases, one or more of these elements were below the level of detection (LOD).

The detector response was checked each day with a NIST 1412 standard reference material (glass) (15). The properties of the filter thickness and detector efficiency were adjusted in the GUPIXwin® (16) program to reproduce the known element concentrations of the NIST standard glass. The spectral fits were always optimized assuming a thick-target option. Additionally, once the energy calibration was established, the fitting program was not allowed to vary these calibration parameters. Finally, it was found that the uncertainties reported by the GUPIXwin® fitting program were often overly optimistic when compared to the actual standard deviation of a set of replicate measurements for a single sample.

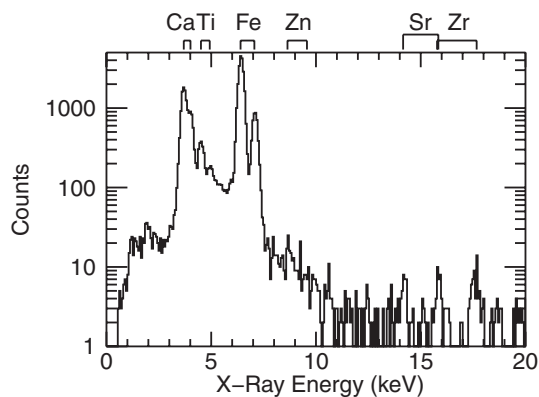


FIG. 1—Typical X-ray spectrum from one of the recovered glass fragments. Selected lines are identified. In this spectrum, a *c.* 500- $\mu\text{m}$  mylar filter was placed between the target and detector to suppress the yield from lighter elements. Some of the elements of interest are clearly below the level of detection for this sample.

Typically, 10 multiple independent runs per sample on at least five different locations on the sample were used to assess experimental standard deviations of the elemental concentrations. A total of 15 samples were collected from the windshields and side windows of various vehicle makes and models at a local scrap yard as well as three reference samples supplied by the Michigan State Police.

### Comparison Protocols

Ideally, the absolute concentrations of the various trace elements in the samples could simply be compared and conclusions drawn about their provenance. Additionally, the ratio of each trace element to a relatively abundant elemental constituent in the glass, such as Ca, could be calculated, and then these calculated ratios in one sample compared to those from another. This ratio approach can minimize the systematic errors found in comparisons of absolute concentrations. One can also renormalize all the trace element concentrations for a sample so that the concentration of a relatively abundant element will match that of the reference sample.

Each of these methods of comparison has certain advantages, and each is susceptible to certain systematic problems. By instituting a three-test protocol that includes each type of comparison listed earlier, the systematic errors of each method are minimized and higher reliability was achieved. It was also more efficient to institute a two-phase approach to the comparison process. The first phase was designed to quickly compare a large number of samples to a single reference sample. After most samples were eliminated as being statistically different from the reference, the few remaining samples were subjected to further, more extensive, testing. Of course, if there was only a small set of samples to compare or if the samples could be presorted by refractive index measurements or other distinguishing characteristics, the process would simply begin with the second phase. In phase I, only one X-ray spectrum is taken for each test sample, but the concentrations of trace elements in the reference sample are measured 10 times at a variety of positions, typically five.

For each test sample, the same three comparisons are performed. Specifically, to compare the absolute concentration of a single trace element, the difference between the average of the reference sample concentration measurements,  $C_r$ , and the single concentration measurement of the  $i$ th test sample,  $C_i$ , was calculated. This difference was normalized based on the error in the mean of the reference sample measurements,  $s_r$ , (standard deviation divided by the square root of the number of measurements  $N$ ) and the estimated error in the single-sample measurement,  $s_i$ , which was taken to be the standard deviation of the reference sample measurements. This characterization of the difference (normalized difference) was calculated from

$$(C_r - C_i) / \sqrt{s_r^2 + s_i^2}$$

As discussed earlier, GUPIXWin<sup>®</sup> often underestimates the concentration uncertainty so that for the single-sample measurements, the reference sample standard deviation from a series of measurements of the reference sample was adopted as a better estimate of the true error of a single measurement even though it is based on a different actual sample. In short, the standard deviation from the multiple measurements of the single reference standard is adopted for all the samples to reduce processing time. If all the systematic variability could be eliminated and the standard deviations were the same from sample to sample, then the normalized difference could be interpreted (in general statistical terms) where a large absolute

value would imply a large probability that the hypothesis, that the data from the two samples have the same distribution, is false. In the strictest terms, a large absolute normalized difference does not speak directly to the provenance of two samples, yet this is what is assumed as conclusions about provenance are made. In this case, a (somewhat arbitrary) value of  $\pm 3$  was set as the dividing line above which the concentration in the sample and the concentration in the reference are taken to be different. This cutoff, as well as those that follow, was chosen to minimize false negative conclusions when comparing multiple measurements of a single piece of glass. This normalized difference is calculated and tabulated for each trace element. Future studies are planned with greatly expanded sample sizes that would allow for the limit to be set more quantitatively to minimize the number of samples needing more testing while maintaining reliability.

One can also form ratios of the various trace element concentrations for a single sample and the reference sample and then compare the difference in the ratios (with appropriate normalization). The number of all possible ratios in this case, starting with nine trace elements, would be 36. However, many of these ratios have such large uncertainties that they carry no information. Thus, only ratios involving the most abundant five trace elements in the reference sample were calculated resulting in 10 ratios. If one of these elements was weak or missing in the individual sample, the ratios were still calculated. One should note that while we have more values to compare (10 ratios vs nine absolute concentrations), the information content is actually reduced because each individual concentration is used in multiple ratios. A normalized difference can be calculated for this test. Rather than calculate the error in any ratio by propagating the GUPIXWin<sup>®</sup> concentration error, the standard deviation of each ratio was calculated based on the multiple measurements of the reference sample. The mean ratio for each element combination was calculated, and then a normalized difference score was found with the same approach as in the first test. For these comparisons, a normalized difference of  $\pm 2$  was taken as the dividing line above which the concentration in the sample and the concentration in the reference are taken to be different. The dividing line was lowered because, in principle, there is less systematic error when ratios of concentrations are compared. This dividing line is also somewhat arbitrary pending studies with larger sample sets.

The third comparison was based on normalizing all the measured trace element concentrations so that one element, typically Ca, in an individual sample matched the average concentration of the reference sample. A normalized difference was calculated as for the absolute concentration comparisons except that the element used for normalization is no longer used. The dividing line between samples that need additional testing and those that are clearly different here was set at a normalized difference value of  $\pm 4$ . Again, this will be refined in future studies. While each of these normalized difference values was set arbitrarily to different numerical values to optimize the discrimination possible in these samples, their actual values are not critical to prove the efficacy of the method under development. When larger data sets become available, a common value for all three tests might be adopted and used as a "traditional" value to assist with interlaboratory comparisons.

As this approach was developed, it became necessary to deal with cases where a particular trace element was present in one sample but not in the glass piece to which one was comparing (given all comparisons are performed pairwise). Additionally, there were cases where the measured concentration of a particular trace was low and near the LOD. It is easy to draw conclusions when the concentration of an element in one sample is high and in

another it is below the LOD. This indicates a significant difference. If the two samples being compared both have concentrations below the LOD, then one really has weak information. This would be the case for two samples from a common source; this could be the case for two samples from different sources just by chance, and this could be the case for two samples from different sources which would be statistically different if the LOD were lower. Because of these ambiguities, we did not use these comparisons when making a conclusion that two fragments were different. If the concentrations are near the LOD, then care is needed. For the absolute comparison and the normalized comparison (the first and third tests), either the reference sample or the test sample had to have a valid measurement of the particular element. For a test sample (measured once), a valid measurement means that the measured concentration was found to be greater than the LOD reported by GUPIXWin<sup>®</sup>, and for the reference sample, more than half of the measured concentrations were required to be greater than the LOD. For the comparison of ratios (second test), which involve two elements and two samples, again either the reference or test sample had to have a valid ratio. For the test sample ratio to be considered valid, both elements involved in the ratio had to have concentrations greater than the LOD, and for the reference sample, both elements involved in the ratio had to have more than half of the measurements greater than the LOD. Element comparisons that were not valid (where the measured result for an elemental comparison of both of the two fragments being compared had few or no measurements above LOD) were simply not used to conclude that a pairwise comparison indicated a difference. The valid comparisons from other trace elements were still examined and form the basis of any conclusions.

Once the normalized difference scores for each of the comparisons made for each test sample were tabulated (with invalid scores owing to measurements falling below the LOD removed), one can eliminate those samples that are clearly different from the reference sample and move on to additional testing of those that appear indistinguishable in this preliminary characterization. If a particular test sample had a normalized difference score within the cutoff value ( $\pm 3$  for the absolute comparisons,  $\pm 2$  for the ratio comparisons, and  $\pm 4$  for the normalized test) for all the elements or ratios for any one of the comparison methods, that test sample entered phase II for further testing. The remaining samples were designated to be from a different source than the test sample and were not subjected to additional testing. In other words, if all three types of tests yielded a clear indication that the two samples being compared are different (all the comparisons for the particular type of test greater than the threshold value), no additional testing was carried out.

Phase II testing of samples is essentially the same protocol as phase I except that now both the reference sample and the test sample were subjected to at least 10 independent measurements. The various comparisons were performed by calculating the well-defined Student's *t*-test score

$$t_i = (C_r - C_i) / S_{C_r - C_i}$$

where

$$S_{C_r - C_i} = \sqrt{\{[(N_r - 1)s_r^2 + (N_i - 1)s_i^2] / (N_r + N_i - 2)\} (1/N_r + 1/N_i)},$$

$C_r$  and  $C_i$  are the average concentrations (or ratios) of the reference and test sample,  $N_r$  and  $N_i$  are the number of measurements of each sample, and  $s_r$  and  $s_i$  are the standard deviations for the set of measurements. For the ratio tests, the logarithm of each ratio,

which sometimes has a positive skew to their distribution, was also calculated and used to compare. The final results were not affected. In this study, no attempt was made at a multivariate analysis (such as a Hotelling *t*-test), because the comparisons always just involve just two fragments rather than pairs of fragments from large sample sets. If any one-dimensional comparison of any single element indicates a difference, then the concentrations, and hence samples, are considered to be different. This could result in cases where a number of individual element comparisons are all somewhat different so that the totality of the measurements should be considered as giving different concentrations for the two samples, but because no single one is over threshold, the wrong conclusion is made. For the 18 samples reported in this paper, analyzed by the method outlined here, this was never observed, but this will be investigated again in future work that has a larger sample size. (The statistical tests performed here are much more simplistic than those discussed in references [17–19] but given the small sample size and the focus on PIXE for measurement, the simple approach is adequate to evaluate the technique's promise.)

Valid measurements for either the reference or test samples again require that over half of the concentrations are found to be greater than the LOD reported by GUPIXWin<sup>®</sup>. To conclude that a particular sample is different from the reference sample, the phase II protocol requires that the *t*-test scores for all three types of comparisons for all the valid elements (or ratios) are greater than the chosen limits of  $\pm 3.5$  for all three types of comparison at this phase. (Again, future studies of larger sample sets could refine this common limit.) If any of the comparisons did not exceed these pseudo-*t* values, then the samples were considered indistinguishable. This does not mean that the samples actually did come from the same original source because it is possible for two pieces of glass from different sources to have the same trace element concentrations by chance. Thus, we label these test samples as indistinguishable rather than using the nomenclature of "same." If any of the three tests, which treat systematic errors differently, conclude the samples are indistinguishable, then they are characterized as indistinguishable even though other tests may yield *t*-test values greater than the cutoff. (Note that if the number of samples is small, one would simply start with phase II testing.)

In both the phase I and phase II testing, there was no consideration of possible element correlations. Both Ca and Sr have similar trace element chemistry, and the concentrations might be expected to rise or fall together (17–19), for example. We do not have to directly factor this into any of the decisions made because our basic approach is to look for significant differences within pairs of samples. If two elements are correlated, and both are significantly different from concentrations in a second sample, then the conclusion is still that the concentrations are different. If only one of the correlated elements is different, the conclusion is still that the concentrations of the two samples are different. If there are extensive elemental correlations among the nine elements measured in this test, which was not observed for this small sample set, then the power to discriminate between samples will obviously be diminished. This will be more carefully examined in a larger data set, and highly correlated elements concentrations can be removed from the comparisons.

## Results and Discussion

After this comparison protocol was established, it was tested against two sample sets. The smaller set consisted of three small irregular glass fragments (on the order of millimeters in size) provided by the Michigan State Police forensic laboratory. These

fragments were from automobile windshield glass samples used in the laboratory to train evidence examiners. The second set was a collection of 15 samples of auto windshield and headlight glass that were collected from a variety of vehicles at a local salvage yard. These samples ranged in size from a few millimeters to tens of millimeters. For testing purposes, one of the larger samples was divided into three with one piece becoming the reference sample to which all others were compared and the other two pieces of that fragment were added to the pool of test samples. This creation of a data set of 16 samples was carried out in a double-blind method from the perspective of the sample preparation, data acquisition, and analysis. As indicated earlier, the larger sample set was subjected to a two-phase testing protocol while the smaller set was only subjected to the phase II protocol. The absolute elemental concentrations measured for a representative subset of samples are shown in Table 1, for both phase I and phase II testing. The elemental concentrations are typical of float glass used in automobiles, and the typical precision of the PIXE measurements obtained in this study is evident in this table.

The phase I protocol detailed earlier was followed, and six of the samples were within the cutoff limits for all three tests. These six samples were then subjected to phase II testing. Table 2 shows the individual test conclusions and the overall match conclusion for these six samples. Those cases where every test indicated that the samples came from different primary sources were considered different and not from the same original source. The remaining two, samples 9 and 12, were considered to be "not different." Either they did come from the same source or by chance they had the same characteristics. After the double-blind analysis was performed, it was then confirmed that these two were the two pieces that did come from the same source as the reference sample. One should note that sample 9 actually had comparisons outside the established limits for the absolute comparison of concentrations. Given that our protocol requires all three tests to be different to draw that conclusion, sample 9 was assigned to the not-different category on the basis of the other two comparisons.

A similar phase II study of three samples from the Michigan State Police was carried out. One sample of this set was obviously different by every measure. In fact, even without statistical tests, it was obvious that this piece was different simply because the raw spectra basically showed a number of elements that were not present in the others. Comparisons of the other samples resulted in a conclusion that they were not different. However, here too, this was based on finding them not-different with the Ca-normalized test and the ratio test. The absolute concentration test had comparisons that were outside the protocol limit for that type of test.

## Conclusion

The protocol described here was found to give the correct known answer for the characterization of glass fragments. Of course, it would be naive to assume that in a huge sample set, there would be no false positives or false negatives. The rate of such occurrences can be simulated, but only if the distribution of trace elements in random collections of auto glass is known. This long-term study of the false determinations is underway but requires a much larger sample set to truly quantify the trace element distributions so that simulations are accurate. Work is also underway to test the protocols described here against a set of 80 auto glass samples from the Federal Bureau of Investigation. This larger sample set will also be useful for a better understanding of appropriate decision limits.

TABLE 1—Representative measured elemental concentrations (in percent by weight) used in the analysis of the glass samples. For the nine elements analyzed in this study, the first three rows represent typical phase I testing, where the reference line is the average of 10 independent measurements of the reference sample, and sample 3 and sample 12 are single measurements of representative samples that passed and failed the phase I criteria, respectively. The numbers in bold are elemental concentrations that were outside comparison limits for absolute concentration comparisons. The last two rows of the table represent phase II testing for the reference and sample 12, where 10 independent replicate measurements of each sample were made. Sample 12 passed the absolute elemental concentration comparison test on phase II testing as well. The elemental concentrations in italics were at or below level of detection (LOD) statistics and were not used in the discrimination protocol. To minimize any systematic errors, replicates of the reference sample were redone in phase II along with replicates of samples rather than relying on results from phase I testing. Typical LOD concentrations are shown in parentheses in the first row.

Percent by Weight (LOD)	Ca (0.06)	Ti (0.011)	Cr (0.005)	Mn (0.004)	Fe (0.0015)	Cu (0.0015)	Zn (0.002)	Sr (0.003)	Zr (0.005)
Reference	9.25 ± 0.04	1.48 ± 0.12 × 10 <sup>-2</sup>	4.60 ± 0.44 × 10 <sup>-3</sup>	3.48 ± 0.30 × 10 <sup>-3</sup>	3.90 ± 0.01 × 10 <sup>-1</sup>	1.38 ± 0.10 × 10 <sup>-3</sup>	1.27 ± 0.14 × 10 <sup>-3</sup>	4.50 ± 0.71 × 10 <sup>-3</sup>	1.05 ± 0.11 × 10 <sup>-2</sup>
Sample 12	9.27 ± 0.14	1.07 ± 0.38 × 10 <sup>-2</sup>	5.89 ± 1.34 × 10 <sup>-3</sup>	2.72 ± 0.95 × 10 <sup>-3</sup>	3.97 ± 0.03 × 10 <sup>-1</sup>	1.57 ± 0.33 × 10 <sup>-3</sup>	0.70 ± 0.38 × 10 <sup>-3</sup>	3.06 ± 2.22 × 10 <sup>-3</sup>	1.09 ± 0.35 × 10 <sup>-2</sup>
Sample 3	8.57 ± 0.14	<b>9.55 ± 0.38</b> × 10 <sup>-2</sup>	6.54 ± 1.34 × 10 <sup>-3</sup>	1.07 ± 0.95 × 10 <sup>-3</sup>	<b>4.60 ± 0.03</b> × 10 <sup>-1</sup>	1.80 ± 0.33 × 10 <sup>-3</sup>	1.55 ± 0.38 × 10 <sup>-3</sup>	1.23 ± 2.22 × 10 <sup>-2</sup>	1.80 ± 0.35 × 10 <sup>-2</sup>
Reference (phase II)	9.34 ± 0.05	1.14 ± 0.06 × 10 <sup>-2</sup>	4.88 ± 0.34 × 10 <sup>-3</sup>	3.76 ± 0.26 × 10 <sup>-3</sup>	4.02 ± 0.01 × 10 <sup>-1</sup>	1.30 ± 0.13 × 10 <sup>-3</sup>	1.35 ± 0.13 × 10 <sup>-3</sup>	4.64 ± 0.35 × 10 <sup>-3</sup>	1.27 ± 0.11 × 10 <sup>-2</sup>
Sample 12 (phase II)	9.44 ± 0.05	1.34 ± 0.11 × 10 <sup>-2</sup>	4.55 ± 0.36 × 10 <sup>-3</sup>	4.03 ± 0.36 × 10 <sup>-3</sup>	4.04 ± 0.01 × 10 <sup>-1</sup>	1.41 ± 0.10 × 10 <sup>-3</sup>	0.98 ± 0.06 × 10 <sup>-3</sup>	4.76 ± 0.41 × 10 <sup>-3</sup>	1.21 ± 0.11 × 10 <sup>-2</sup>

TABLE 2—Summary of results for each type of comparison and the final conclusion for each sample that was compared in phase II. Of the 16 initial glass samples, only six were identified for the more extensive phase II testing after comparison to the reference sample in phase I, and four of these samples (1,4,14,16) were identified as different by every measure after phase II. Note that using absolute concentrations alone, sample 9 might have been ruled as different as well, but the other two comparison tests of elemental ratios and Ca-normalized ratios failed to distinguish sample 9 from the reference, so it was ruled Not Different.

Sample	Absolute	Ratio	Ca normalized	Conclusion
1	Different	Different	Different	Different
4	Different	Different	Different	Different
9	Different	Not different	Not different	Not different
12	Not different	Not different	Not different	Not different
14	Different	Different	Different	Different
16	Different	Different	Different	Different

This initial trace element analysis of glass with PIXE is shown to be a promising method of comparing glass samples. The testing protocol, including a two-phase approach, did achieve sufficient reliability to distinguish samples in a double-blind test. Advantages of the PIXE approach compared to XRF and LA-ICP-MS include the nondestructive nature, the ease and speed with which measurements can be made, and sensitivity to elements with higher atomic number, and sampling to a greater depth to avoid surface effects. It is especially important to note that the nondestructive nature of PIXE also allows this technique to be used together with more sensitive techniques. The most likely possibility for routine forensic use of this “niche” technique will come after the establishment of a rigorous measurement protocol for the analysis of the repeated X-ray analysis via PIXE. If a laboratory develops the method described here with a large data set and determines the precise limits on type-1 and type-2 errors that arise, then it is important to note that a pair of glass samples could be submitted to this laboratory for analysis, and the entire sample preparation, data acquisition, and data analysis could be performed in an hour or two. If the samples were shown to be distinct by the inclusion of trace element measurements possible by PIXE, considerably more time-consuming trace element analysis by more sophisticated and destructive techniques could be avoided.

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