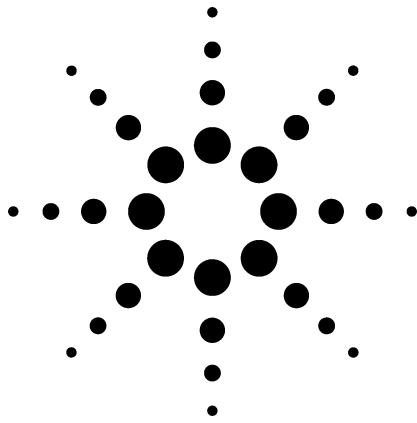


# Analysis of Forensic Glass Samples by Laser Ablation ICP-MS

Application



Forensics

## Author

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## Abstract

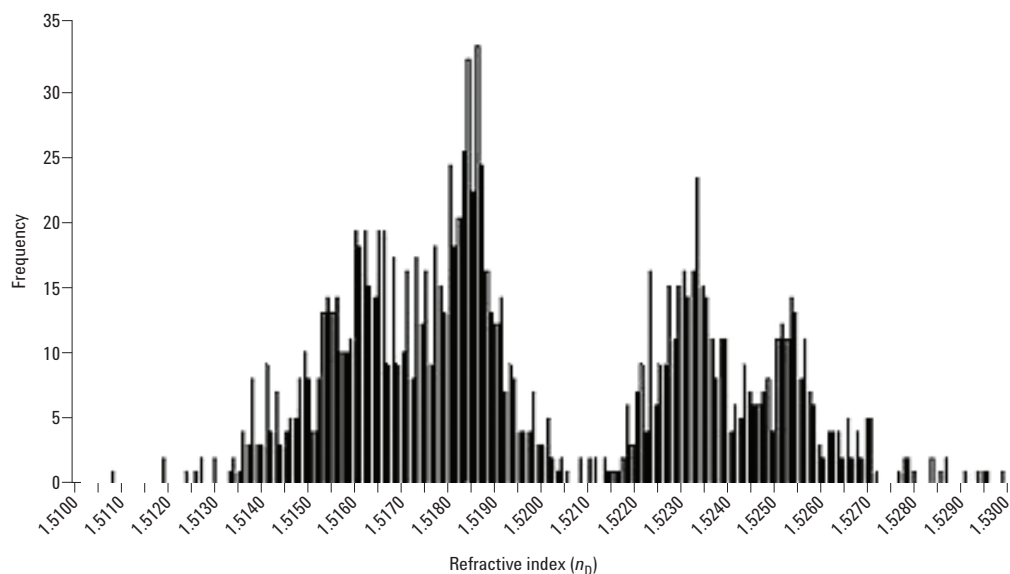
**Physical evidence is often distributed widely when a crime is being committed. The smaller these suspect materials are, the more likely they will be transported from the crime scene undetected. When glass is shattered, the fragments created can be less than a few hundred microns (<0.2 mm). These fragments can become attached to clothing and embedded in shoes, "tagging" the criminal with a unique marker. However, as the major and minor elemental composition of modern glass is becoming more difficult to discriminate using traditional methods, new instrumentation is needed capable of resolving differences in the trace elemental profiles of similar glasses. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was evaluated and found to provide the accuracy, sensitivity and spatial resolution necessary for this application.**

## Introduction

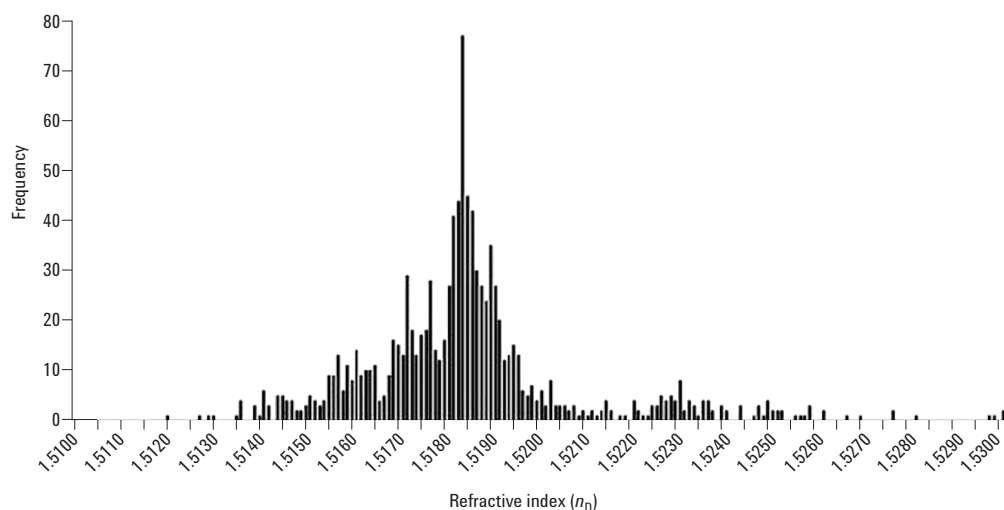
Traditional methods of forensic glass analysis include the determination of a number of physical properties, including refractive index (RI), wet chemistry, scanning electron microscopy (SEM), x-ray fluorescence (XRF), and optical microscopy [1]. Although these techniques offer a high degree of differentiation with traditional glass, modern glass has a greater degree of chemical and physical similarity. The major and minor elemental composition and RI values of these new materials are becoming more difficult to discriminate. The histograms in Figures 1a and 1b show RI values for flat glass extracted from an FBI database for the periods of 1964 to 1979 and 1980 to 1997 respectively [2]. Comparison of the two charts clearly shows the reduced opportunity for intersample discrimination using this technique. Although the major and minor elemental composition of these glasses are very similar and therefore difficult or impossible to discriminate, using traditional methods of characterization, these glasses may have trace elemental signatures which are distinguishable by LA-ICP-MS.



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**Figure 1a. Distribution of RI values from FBI database of flat glasses, 1964 to 1979.**



**Figure 1b. Distribution of RI values from FBI database of flat glasses, 1980 to 1997.**

### Instrumentation

All the analyses for these experiments were undertaken using an Agilent 7500s ICP-MS. Solid sampling was achieved by introducing a stream of particles generated *in-situ* by direct coupling of a short ultraviolet (UV) laser with the sample surface

into the ICP using a stable flow of argon gas. The laser system used was a New Wave Research (Fremont, CA) UP-213AI Nd:YAG operating at the 5th harmonic frequency (213 nm). Operating parameters for each experiment are given in Table 1. For more information on LA-ICP-MS, see Reference 3.

## Operating Parameters

### Glass Fragments

**Table 1. LA-ICP-MS Operating Conditions**

| Laser            |                    | ICP-MS       |                              |
|------------------|--------------------|--------------|------------------------------|
| Line ablation    |                    | RF Power:    | 1200 W                       |
| Spot size:       | 100 $\mu\text{m}$  | Plasma gas:  | 14 L/min                     |
| Line length:     | 350 $\mu\text{m}$  | Carrier gas: | 0.8 L/min                    |
| Power:           | 2 mJ               | Acquisition: | Time Resolved Analysis (TRA) |
| Stage speed:     | 20 $\mu\text{m/s}$ | Integration: | 10 ms                        |
| Pulse frequency: | 10 Hz              | Masses:      | 36                           |
|                  |                    | Acquire time | 114 s                        |

## Experimental

Calibration of the LA-ICP-MS was carried out using the following standard, obtained from National Institute of Science and Technology (NIST), USA:

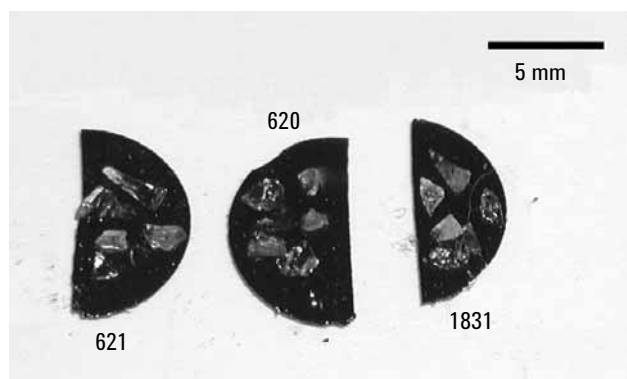
NIST SRM 612: 50  $\mu\text{g/g}$  nominal trace element concentration.

Matrix elements: Si ( $\text{SiO}_2$ ), Na ( $\text{Na}_2\text{O}$ ), Ca ( $\text{CaO}$ ), Al ( $\text{Al}_2\text{O}_3$ )

NIST soda lime glass standards (620, 621 and 1831) were used as surrogates for float glass (flat, clear glass) samples. It was therefore possible to check the accuracy and the precision of the calculated values by comparing them with the certified values given for the major elements (Table 2). Each sample was placed in a separate, sealed plastic bag and shattered. The small fragments (0.5 mm to 2 mm) were attached to a petrographic slide using double-sided graphite tape (Figure 2). This process was repeated for all the surrogates, as well as the three headlamp samples.

**Table 2. NIST SRM 612 Major and Trace Multi-Element Results**

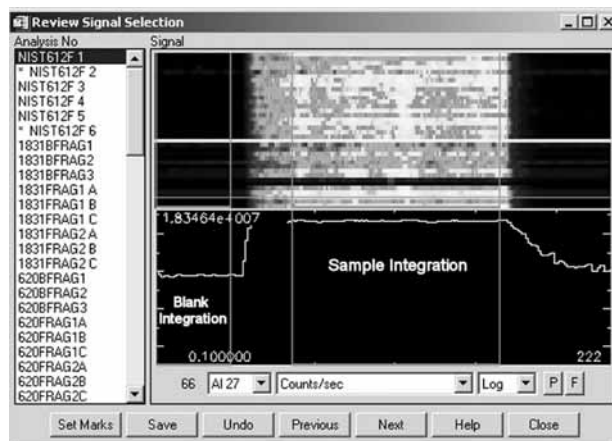
| Element    | Na 23 | Mg 24 | Al 27 | Ca 44 | Ti 47 | Cr 52 | Mn 55  | Fe 57  | Ni 60  | Zn 66  |
|------------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|
| Mean, ppm  | 10.4% | 79.07 | 1.1%  | 8.7%  | 49.5  | 39.8  | 38.5   | 57.7   | 38.8   | 38.6   |
| SD         | 0.2%  | 2.51  | 0.0%  | 0.1%  | 2.52  | 0.30  | 0.49   | 2.99   | 2.02   | 1.50   |
| %RSD       | 1.9   | 3.2   | 0.5   | 1.1   | 5.1   | 0.8   | 1.3    | 5.2    | 5.2    | 3.9    |
| %Agreement | 100.3 | 102.1 | 105.6 | 101.3 | 103.0 | 99.6  | 100.2  | 102.5  | 100.8  | 101.7  |
| Element    | Rb 85 | Sr 88 | Y 89  | Zr 90 | Mo 95 | Ba 38 | Ce 140 | Hf 178 | Pb 208 | Th 232 |
| Mean ppm   | 32.1  | 77.0  | 38.7  | 36.3  | 38.7  | 38.0  | 38.5   | 34.5   | 36.2   | 36.9   |
| SD         | 0.42  | 0.94  | 0.95  | 0.97  | 0.81  | 0.60  | 0.53   | 1.01   | 5.06   | 1.15   |
| %RSD       | 1.3   | 1.2   | 2.4   | 2.7   | 2.1   | 1.6   | 1.4    | 2.9    | 14.0   | 3.1    |
| %Agreement | 101.5 | 101.1 | 101.0 | 100.8 | 101.0 | 100.6 | 100.5  | 99.2   | 92.9   | 99.1   |



**Figure 2. Sample mounting of glass fragments.**

NIST 612 standard glass was used as a means of calibration and was analyzed repeatedly throughout the analysis procedure, bracketing each sample set. Each sample analysis was 115 seconds and consisted of a 20-second blank delay, a 60-second laser sampling period, followed by a 35-second washout period. Six repetitive data acquisitions over two separate lines were collected for each sample. The data was imported into Glitter™ data reduction software (Macquarie University - GEMOC). Analyte and blank regions were defined

within the Signal Selection Screen (Figure 3) and quantitative values were determined. The mean and standard deviation (SD) for each sample was then calculated (Table 3a).



**Figure 3. Signal selection screen, Glitter data reduction software.** Traditionally used in geochronology, forensic data benefits from the ability of this software to enable easy isolation of changing data sets within a heterogeneous sample matrix. Each sample has its own associated blank, reducing memory effects.

**Table 3a. Glass Data Obtained From the Analysis of Standard Glass Fragments**  
Unless Otherwise Noted all Data is in µg/g (ppm)

| Element | NIST 620   |          |         |               | NIST 621   |          |         |               | NIST 1831  |          |         |               |
|---------|------------|----------|---------|---------------|------------|----------|---------|---------------|------------|----------|---------|---------------|
|         | Mean (ppm) | SD (ppm) | RSD (%) | Agreement (%) | Mean (ppm) | SD (ppm) | RSD (%) | Agreement (%) | Mean (ppm) | SD (ppm) | RSD (%) | Agreement (%) |
| Na 23   | 10.8%      | 0.33%    | 3.1     | 100.7         | 9.3%       | 0.39%    | 4.2     | 98.0          | 9.8%       | 0.33%    | 3.4     | 100.9         |
| Mg 24   | 3.1%       | 0.05%    | 1.5     | 140.2         | 0.2%       | 0.003%   | 1.5     | 136.1         | 2.9%       | 0.038%   | 1.3     | 137.3         |
| Al 27   | 1.0%       | 0.02%    | 1.8     | 107.3         | 1.6%       | 0.01%    | 0.6     | 108.8         | 0.66%      | 0.004%   | 0.6     | 102.7         |
| Ca 44   | 5.0%       | 0.09%    | 1.8     | 99.0          | 7.7%       | 0.11%    | 1.4     | 100.2         | 5.7%       | 0.064%   | 1.1     | 96.6          |
| Ti 47   | 105        | 2.245    | 2.1     | 97.1          | 86         | 1.28     | 1.5     | 102.7         | 118        | 1.77     | 1.5     | 103.4         |
| Cr 53   | 2.02       | 0.297    | 14.7    | –             | 3.97       | 0.29     | 7.2     | –             | 2.13       | 0.19     | 9.1     | –             |
| Mn 55   | 13.9       | 0.261    | 1.9     | –             | 17.9       | 0.31     | 1.7     | –             | 12.8       | 0.15     | 1.2     | –             |
| Fe 57   | 203        | 3.310    | 1.6     | –             | 210        | 2.04     | 1.0     | –             | 397        | 5.89     | 1.5     | –             |
| Ni 60   | 0.49       | 0.049    | 10.0    | –             | 1.80       | 1.13     | 62.8    | –             | 0.57       | 0.21     | 37.3    | –             |
| Zn 66   | 6.7        | 0.265    | 3.9     | –             | 2.76       | 0.17     | 6.1     | –             | 8.4        | 0.61     | 7.3     | –             |
| Rb 85   | 5.3        | 0.197    | 3.7     | –             | 38.2       | 1.23     | 3.2     | –             | 6.03       | 0.16     | 2.6     | –             |
| Sr 88   | 286        | 4.709    | 1.6     | –             | 106        | 1.44     | 1.4     | –             | 89.9       | 1.21     | 1.3     | –             |
| Y 89    | 2.99       | 0.043    | 1.5     | –             | 2.63       | 0.05     | 1.9     | –             | 2.05       | 0.04     | 1.8     | –             |
| Zr 90   | 198        | 4.291    | 2.2     | –             | 62.7       | 0.96     | 1.5     | 120.9         | 39.5       | 0.93     | 2.3     | –             |
| Mo 95   | 0.19       | 0.022    | 11.6    | –             | 2.34       | 0.13     | 5.7     | –             | 0.18       | 0.01     | 6.9     | –             |
| Ba 138  | 22.5       | 0.156    | 0.7     | –             | 84.7       | 7.41     | 0.9     | –             | 30         | 0.54     | 1.8     | –             |
| Ce 140  | 2.50       | 0.036    | 1.4     | –             | 2.09       | 0.03     | 1.4     | –             | 4.35       | 0.08     | 1.8     | –             |
| Hf 178  | 4.30       | 0.106    | 2.5     | –             | 1.51       | 0.02     | 1.1     | –             | 0.97       | 0.03     | 3.5     | –             |
| Pb 208  | 1.97       | 0.138    | 7.0     | –             | 14.5       | 0.96     | 6.6     | –             | 1.94       | 0.10     | 5.1     | –             |
| Th 232  | 0.40       | 0.002    | 0.6     | –             | 0.62       | 0.00     | 0.4     | –             | 0.60       | 0.01     | 0.9     | –             |

**Table 3b. Glass Data Obtained from Headlight Fragments**Unless Otherwise Noted all Data is in  $\mu\text{g/g}$  (ppm)

| Element | Fragment Sample A<br>(Sylvania Headlamp H6024CB) |        |       | Fragment Sample B<br>(Sylvania Headlamp H4656) |       |       | Fragment Sample C<br>(Sylvania Headlamp 5006) |       |       |
|---------|--|--------|-------|--|-------|-------|---|-------|-------|
|         | Mean   | SD     | RSD   | Mean   | SD    | RSD   | Mean  | SD    | RSD   |
|         | (ppm)  | (ppm)  | (%)   | (ppm)  | (ppm) | (%)   | (ppm)   | (ppm) | (%)   |
| Na 23   | 3.5%   | 0.09%  | 2.64  | 34.9%  | 0.54% | 1.54  | 3.59%   | 0.08% | 2.36  |
| Mg 24   | 41.78  | 0.37   | 0.88  | 70.6   | 0.96  | 1.36  | 62.8  | 0.55  | 0.88  |
| Al 27   | 1.2%   | 0.04%  | 3.10  | 1.0%   | 0.01% | 1.00  | 1.04%   | 0.01% | 0.70  |
| Ca 44   | 153  | 29.23  | 19.12 | 221  | 14.59 | 6.60  | 200   | 34.29 | 17.16 |
| Ti 47   | 71   | 5.19   | 7.31  | 46.3   | 0.97  | 2.10  | 44.5  | 0.71  | 1.60  |
| Cr 53   | 1.26   | 0.29   | 23.08 | 2.19   | 0.36  | 16.39 | 2.13  | 0.26  | 12.15 |
| Mn 55   | 2.67   | 0.06   | 2.07  | 1.29   | 0.10  | 8.10  | 1.20  | 0.03  | 2.34  |
| Fe 57   | 96   | 1.85   | 1.93  | 234  | 4.15  | 1.78  | 237   | 4.23  | 1.78  |
| Ni 60   | 0.43   | 0.06   | 13.61 | 0.32   | 0.05  | 15.09 | 0.27  | 0.08  | 27.36 |
| Zn 66   | 1.44   | 0.13   | 9.02  | 1.01   | 0.10  | 9.80  | 0.89  | 0.16  | 18.42 |
| Rb 85   | 0.38   | 0.01   | 3.81  | 0.38   | 0.01  | 2.43  | 0.40  | 0.01  | 3.60  |
| Sr 88   | 4.08   | 0.11   | 2.58  | 5.16   | 0.10  | 2.00  | 3.95  | 0.10  | 2.44  |
| Y 89    | 9.42   | 1.27   | 13.50 | 0.92   | 0.03  | 2.84  | 0.86  | 0.03  | 3.38  |
| Zr 90   | 5099   | 711.55 | 13.95 | 119  | 4.62  | 3.88  | 97  | 5.95  | 6.12  |
| Mo 95   | 3.28   | 0.11   | 3.37  | 0.69   | 0.08  | 11.48 | 0.53  | 0.06  | 11.87 |
| Ba 138  | 4.42   | 0.09   | 1.97  | 1.86   | 0.05  | 2.52  | 1.82  | 0.04  | 2.10  |
| Ce 140  | 3.09   | 0.15   | 5.02  | 3.79   | 0.06  | 1.58  | 3.57  | 0.06  | 1.71  |
| Hf 178  | 113  | 15.85  | 14.01 | 2.96   | 0.13  | 4.29  | 2.23  | 0.15  | 6.76  |
| Pb 208  | 0.41   | 0.03   | 6.21  | 0.42   | 0.01  | 2.46  | 0.36  | 0.02  | 5.67  |
| Th 232  | 1.74   | 0.22   | 12.71 | 0.29   | 0.01  | 2.08  | 0.25  | 0.01  | 2.93  |

## Results

### Discrimination of Clear Glass Fragments

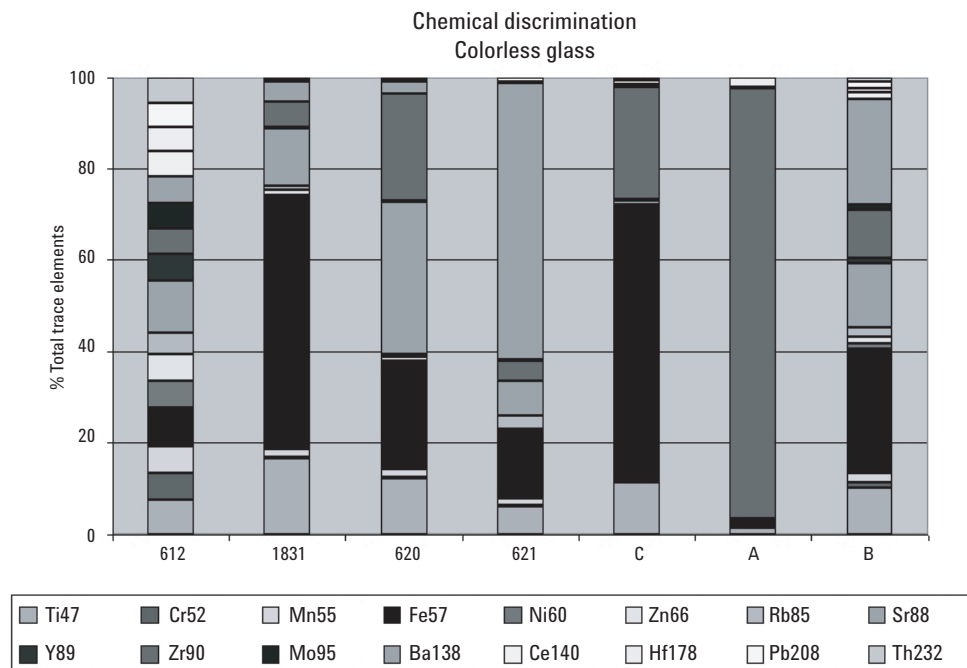
Three sets of automobile headlamp fragments and three sets of NIST soda lime glass standard fragments were chosen as forensic sample surrogates for this study. All glass samples were colorless to the naked eye. Time resolved data was imported directly into Glitter data reduction software from the Agilent 7500s ICP-MS ChemStation software. Blank and sample integration areas were defined within the Signal Selection screen (Figure 3) and elemental concentrations were calculated using NIST 612 as the multi-element standard (Table 2). Though the glass fragments were typically <1 mm, elemental recoveries for the NIST certified values were very good and RSDs were <3% for many elements.

NIST soda-lime glass standards 620 (flat glass), 621 (container glass), and 1831 (sheet glass) were used to emulate samples. The good agreement between the certified values and the returned values support the efficacy of the method used. Though the Mg values are consistently high by approximately 40%, the data suggests that this is likely due to a problem with the calibration standard either because of an inhomogenous distribution of the element, or even possibly variation in the certified value. In this study, the value

for Mg in NIST 612 was defined as 77.44  $\mu\text{g/g}$ ,  $1\sigma$  30.15  $\mu\text{g/g}$  (Pearce, et al 1997) [4]. Another study (Gao, et al 2002) published the NIST 612 Mg value as 64  $\mu\text{g/g}$ ,  $1\sigma$  6  $\mu\text{g/g}$  [5].

Forensic data must be presented in the most accurate and clearly understandable format. Jurors with little or no scientific background must be able to decipher subtle chemical differences between evidentiary materials. Consequently, we have presented our glass data in two discriminating formats: numerically and stacked bar graphs (Tables 3a and 3b and Figure 5). Stacked bar graphs are extremely effective in comparing different multi-component data sets. We have therefore included the quantitative mean values with  $1\sigma$  SD (Tables 3a and 3b).

Like gel electrophoresis, banding patterns within an elemental data set are easy to visualize and differentiate. Stacked bar charts can clearly characterize the elemental nature of a unique sample type. Notice the clear and even banding pattern of NIST 612 (first bar Figure 5). In NIST 612, all elements with the exception of Sr (76 ppm) are nominally at equal concentration (50 ppm), which the banding pattern clearly portrays. The NIST glass serves not only as a quantitative standard, but also describes the effectiveness of the stacked bar chart in its ability to compare trace element constituents.



**Figure 5.** The mean data from Table 3 is presented in a stacked bar chart format. This visual representation of the data aids data presentation in terms of clarity and relative simplicity.

## Conclusion

LA-ICP-MS is an effective tool for the analysis of forensic glass samples. This technique is particularly useful in overcoming the limitations associated with very small sample types or samples composed of chemically inert materials.

Colorless glass fragments, indistinguishable to the naked eye and chemically identical at the ppm level, may be discriminated with good accuracy and precision, even at sub-millimeter dimensions. Due to the micro-destructive nature of this technique, forensic samples characterized by this method may also be available to alternative analysis if confirmation is required.

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