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Multivariate Pattern Matching of Trace Elements in Solids by Laser Ablation Inductively Coupled Plasma-Mass Spectrometry: Source Attribution and Preliminary Diagnosis of Fractionation

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is used with two variations of principal components analysis (PCA) for objective, routine comparisons of forensic materials without time-consuming and destructive sample dissolution. The relative concentrations of trace elements in a solid sample are examined to provide a “fingerprint” composition that can be used for identification and source matching of the material. Residue samples are matched to bulk materials using PCA. Variation of laser focus and PCA are also used to diagnose the severity of elemental fractionation in two metal samples that are prone to fractionation, brass and steel. Such fractionation remains the most significant limitation for accurate quantitative analyses by LA-ICPMS.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is a rapid and sensitive tool for trace elemental analysis of solids.1–3 Usually, little sample preparation is required, and the ablation process consumes only a minute quantity of material (typically in the ng to μg range). The focused laser beam samples a small region of a solid (craters are typically 10–100 μm in diameter), so site-specific elemental distributions can be determined. Since the first demonstration of LA-ICPMS in 1985,4 this technique has been widely adopted in a variety of research areas, including forensic chemistry;5 geological science;6–9 environmental science;10,11 materials science;12 and polymer chemistry.13

The development of accurate and sensitive analysis methods for trace element detection in solid materials is of great value to forensic investigations, materials development, and safeguards and security of nuclear materials. The trace elemental composition of a solid collected from a crime scene can be determined in order to reliably match the solid evidence to its source material. ICPMS analysis of dissolved samples14–16 and LA-ICPMS have been evaluated for forensic analysis of gold,17,18 precious gems,19,20 and glass.21 The sample types selected for the present study are common to forensic work: plain carbon steels, glass fragments, and copper wire. Steels are composed of iron and manganese as major components, but due to widespread recycling of scrap, the trace elemental composition of an individual batch of steel can be unique. Likewise, typical glasses are composed of silicon, calcium, sodium, aluminum, and oxygen as major components, but the trace elemental composition of an individual glass melt is often unique.

The laser ablation sampling technique provides the advantages of speed (with little or no chemical preparation required), minimal sample consumption, and the specificity afforded by microscale sampling. The good detection limits of LA-ICPMS extend the number of measurable elements to improve the confidence of matching procedures. The techniques investigated in this study permit both spatially resolved sampling of heterogeneous materials and bulk sampling by multiple-shot analysis of large areas for determining average composition. Current methods for solids analysis include X-ray fluorescence, arc or spark ablation of conductors, and sample dissolution followed by ICP-AES or ICPMS. These techniques are either insufficiently sensitive for

trace elemental analysis, not applicable to insulating materials, or destroy the evidentiary material.

A major problem affecting the accuracy of quantification by LA-ICPMS is elemental fractionation: the generation of particulates that yield signals that are either high or low for certain elements compared to the composition of the original solid. Fractionation has been observed for both volatile and refractory elements compared to the composition of the original solid. The inclusion of statistical confidence limits to quantify the degree of fractionation effects and to determine optimal ablation conditions. Russo and co-workers reported that the use of fast (fs) laser pulses also minimizes fractionation. This paper describes a multivariate method to diagnose fractionation in unknown homogeneous samples so that optimal ablation conditions that minimize such effects can be identified.

The PCA modeling technique adopted for this study has been successfully used with a variety of analytical techniques including HPLC, GC/MS, ICP emission spectrometry, and LA-ICPMS. Principal components analysis (PCA) can be used to generate a simple, two-dimensional map that summarizes the principal distinguishing characteristics of two sets of multidimensional data. Unlike ternary plots or other common graphical approaches, the PCA technique eliminates the need for trial-and-error selection of elements for sample differentiation and matching. In this paper, the effectiveness of PCA for the comparison of forensic samples by trace elemental composition was investigated further, using a different graphical approach and the inclusion of statistical confidence limits to quantify the degree of differentiation between samples.

EXPERIMENTAL SECTION

Selection and Preparation of Samples. Three NIST steels (139, 139a, 139b), a multistranded copper wire, and four glass fragments (0.25–5.0 mg each, Illinois State Police Forensic Science Laboratory) were analyzed. Sample fragments were mounted on a small piece of flattened clay on a Teflon stage to prevent sample movement during ablation. Otherwise, no physical or chemical pretreatment of the solids was required prior to laser sampling. A small brass disk and a wafer of NIST 1264a steel were selected to investigate elemental fractionation effects and to determine optimal ablation conditions.

ICPMS. The mass spectrometer was a Thermo Finnigan Element I. This device employs magnetic and electrostatic analyzers configured in a reverse Nier-Johnson geometry to provide both mass and kinetic energy selection. The excellent detection limits (80 pg aqueous 115In), linear dynamic range (>10⁶), sensitivity (S = 10⁹ count s⁻¹ ppm⁻¹ aqueous 115In at low resolution), and stability (0.8% RSD for aqueous 115In over 10 min) of this instrument are particularly favorable for the direct, ultratrace analysis of solid fragments by laser ablation. The ICPMS was operated in either low resolution (R = 300) or medium resolution (R = 4000). The sensitivity in medium resolution is lower than that in low resolution by a factor of 10.

The ICP load coil was “shielded” (CD-1 torch, Thermo Finnigan) to improve the ion transmission. With the shield grounded, the ICP is sustained only by inductive coupling, and the secondary discharge between the ICP and sampling cone is attenuated. Compared to analyses performed with a standard ICP torch, the shielded torch improves sensitivity by a factor of 5–20 (depending upon m/z) while maintaining the extremely low background and high precision of the double-focusing instrument.

Laser Ablation. A CETAC Technologies LSX-100 was used to ablate the solid samples. This ablation system consists of a Q-switched, frequency-quadrupled (266 nm) Nd:YAG laser and an ablation cell mounted on an xyz-translation stage. A charge-coupled device camera with motorized zoom control permits real-time observation of the ablated site on a computer monitor. The laser was operated at its maximum power (3.6 mJ pulse⁻¹) with a repetition rate of 10 Hz. To maximize the absolute quantity of ablated material and minimize the likelihood of elemental fractionation, the UV laser was focused at the sample surface. At this focus position, the visual image was defocused 600 μm below the sample surface because of chromatic aberration in the lens used for both ablation and imaging. The sample stage was rastered along a line perpendicular to the beam at a rate of 50 μm s⁻¹. Typical ablation trenched were ~75 μm wide but varied somewhat depending on the physical properties of the sample matrix and the number of laser repetitions per sample location. The 3.6 mJ pulse energy with a spot diameter of 75 μm yields an estimated maximum fluence of ~80 J cm⁻². This value negles the concentration, focusing optics.

An argon flow rate of 1.3 L min⁻¹ was used to transport the ablated particles to the plasma through a Tygon tube roughly 1.5 m long × 3 mm internal diameter. For the sampling position and power used to operate the plasma, this single gas flow rate maximized atomic ion signals for all the elements and samples measured.

Data Analysis for Comparison of Samples. Given the sequential nature of data acquisition by the mass spectrometer, a set of mass spectral peaks was selected for each particular group of samples. Peaks were selected by first acquiring a low-resolution mass spectrum for each sample in the 4–240 m/z range to identify the unknowns.
Table 1. Isotopes Measured in Each Sample Set for PCA

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Isotopes Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>glasses C1–C4</td>
<td>22Na, 24Mg, 27Al, 40Ca, 42Sc, 48Ti, 51V, 52Cr, 54Mn, 58Fe, 60Co, 67Cu, 69Ga, 75As, 81Rb, 85Sr, 87Sr, 90Zr, 93Nb, 98Mo, 107Ag, 120Sn, 121Sb, 130Te, 139La, 140Ce, 141Pr, 143Nd, 147Pm, 150Nd, 154Tb, 155Eu, 158W, 167Dy, 169Yb, 181Ta, 182Hf, 184W, 187Au, 199Hg, 208Pb, 209Bi, 238U</td>
</tr>
<tr>
<td>NIST SRM 139, 139a, 139b</td>
<td>54Mn, 122Sn, 124Sn, 126Te, 140Ce, 141Pr, 143Nd, 147Pm, 150Nd, 154Tb, 155Eu, 158W, 167Dy, 169Yb, 181Ta, 182Hf, 184W, 187Au, 199Hg, 208Pb, 209Bi</td>
</tr>
<tr>
<td>high-purity copper wire (Figure 4)</td>
<td>51Cr, 55Mn, 60Ni, 107Ag, 208Pb, 209Bi</td>
</tr>
<tr>
<td>brass disk (Figure 5)</td>
<td>63Cu, 66Zn, 107Ag, 120Sn, 208Pb</td>
</tr>
<tr>
<td>NIST SRM 1264a (Figure 6)</td>
<td>32Cr, 55Mn, 60Ni, 61Cu, 62Zn, 90Zr, 92Mo, 93Nb, 98Mo, 107Ag, 120Sn, 121Sb, 130Te, 139La, 140Ce, 141Pr, 143Nd, 147Pm, 150Nd, 154Tb, 155Eu, 158W, 167Dy, 169Yb, 181Ta, 182Hf, 184W, 187Au, 199Hg, 208Pb, 209Bi</td>
</tr>
</tbody>
</table>

The elements present. From this full mass spectrum, small mass windows were then identified to include only those elements present in the particular sample set for data collection. Only peaks whose intensities were greater than three times the background signal were selected. This peak selection approach permitted a more rapid analysis and minimized sample destruction by skipping m/z regions devoid of analyte ions. The selected elements were measured in either low resolution or medium resolution. A total of nine spectra were acquired for each sample by ablating a raster pattern in three spatially resolved areas on a sample and collecting three consecutive mass spectra for each area.

Data preprocessing consisted of peak-area integration, background subtraction, and arranging the data in a form suitable for multivariate analysis. The data were saved as ASCII text and imported into Matlab v 6.1 (the MathWorks, Inc., Natick, MA) for multivariate analysis. PCA for chemical and spectral analysis has been reviewed elsewhere.27 Basically, it is a multivariate data reduction method that examines the variance patterns within a multidimensional dataset. The dimensionality of the data set is reduced while a major portion of the original information is retained. This is accomplished by decomposing the correlation matrix of the variables into a set of axes, principal components, which define the directions of the major variances in the data set. The principal components are linear combinations of the variables, composed of three matrices that define the principal component: scores, loadings, and residuals. These matrices facilitate visualization of the relationships of the samples in the data set and interpretation of the data. Scores describe the variance or relationship among the samples in the data set and represent the contribution of the principal component in each sample. Loadings represent the contribution of the old variables (i.e., the mass peaks) to the principal components and describe which variables (or masses) are responsible for the variance in the masses. The residuals represent random variations within the data set and are generally attributed to noise in the data.

Samples within a particular group were compared by generating a PCA model from the data from one sample. Spectra from other samples in the group were then compared to those in the model. The difference or variance of the sample spectra from the developed model was determined by the Q statistic, which indicates how well each sample conforms to the model. The Q statistic is simply the measure of the difference, or residual, between isotopic signals from one sample and their projection into the PCA model.

Data Analysis for Diagnosis of Fractionation. The effects of laser focal position on the fractionation of Cu, Zn, Ag, Sn, and Pb in a small brass sample were also investigated. In this experiment, the laser power was kept constant. Laser focal position was changed over a range of 900 μm in 50-μm increments. Nine mass spectra were collected per focus position, and a PCA model was generated based upon the combined spectra obtained with the laser focused at −50, 0, and +50 μm. These defocus conditions were selected as the basis for the model because it is believed that this range produces the highest energy density at the sample surface and, presumably, the lowest degree of fractionation.39

RESULTS AND DISCUSSION

Glass Fragment Analysis. Common techniques for glass comparison in forensic laboratories involve the evaluation of physical and optical properties such as thickness, color, density, and refractive index. These techniques, however, are often not sufficient to distinguish glass samples from different sources. Four sets of glass fragments of known composition and typical size (~10 mm2) were provided by the Illinois State Police Forensic Science Laboratory. This was a blind test to investigate whether LA-ICPMS can enhance discrimination between glass samples and, furthermore, if the chemical composition information provided by LA-ICPMS can provide source attribution.

Thirty-two elements were monitored (Table 1). Figure 1 shows the graphical representation of PCA for set C of the glass samples. This plot, known as a score plot, shows the first two principal components obtained by PCA. The numbers in parentheses on each axis are the percent of the variance captured by that principal component. Nine replicates were acquired for each sample. Although differences in chemical composition between the four glasses are slight, the score plot clearly indicates that samples C1 and C2 are significantly different from samples C3 and C4, based upon where the corresponding data points cluster in score space. Furthermore, the score plot also shows that C1 is similar to C2 and that C3 is similar to C4. The points for C1 cluster slightly differently from those for C2, which suggests that these samples are slightly different, as is the case for C3 and C4. However, examination of combinations of the other principal components obtained by PCA could not clearly distinguish C1 from C2 or C3 from C4.

To investigate further whether the PCA method can distinguish two similar sample pairs (i.e., C1/C2 and C3/C4), an alternate approach was explored. Four PCA models were generated; each model was based on one of the glass samples. The other three glasses in the sample set were then compared to that model and the Q-residuals for the compared samples were calculated. A graphical representation of this comparison approach is presented in Figure 2. The short horizontal lines at a Q-residual value of ~10 indicate the 95% confidence level for the corresponding model. The plotted points are the average Q-residual values for the nine replicates for each sample set. Data points falling above the 95% confidence level indicate that that sample is dissimilar from the model within 95% confidence. In contrast, data points falling below this level cannot be differentiated from the model at the 95% confidence limit. It is interesting to note that samples C1 and C2 have comparable Q-residual values when compared to the models generated by samples C3 and C4 (and vice versa), as expected from the score plot approach (Figure 1).

Figure 2 clearly shows that despite the close chemical similarity of the four glass samples (particularly the C1/C2 and C3/C4 pairs), all four of these glasses are dissimilar at the 95% confidence level. This analysis is in agreement with the known origins of the samples. The pairs C1/C2 and C3/C4 are similar, but all are from different suppliers.

NIST Steels. To further investigate the utility of the multivariate LA-ICPMS technique on samples with even greater similarity, three low-alloy steels were chosen for analysis (NIST 139, 139a, and 139b). For this analysis, 20 elements were measured (Table 1) and 9 replicates were again collected for each sample. The data sets were analyzed using the sample and PCA model comparison approach described above.

Figure 3 shows the Q-residual value for each replicate of NIST 139 and NIST 139b compared to the PCA model for NIST 139a. The dashed line indicates the 95% confidence level calculated for the NIST 139a PCA model. All but one replicate for NIST 139 lies above the 95% confidence level. Thus, NIST 139 is likely not from the same source as NIST 139a. One replicate falls within the statistical definition of the 95% confidence level; i.e., 1 in 20 samples will lie outside the expected average range.

Similarly, all but one replicate of the NIST 139b data set lies below the 95% confidence limit. This indicates that NIST 139b and NIST 139a cannot be distinguished at the 95% confidence level and could be from the same source. These PCA results are corroborated by subsequent information from the supplier of these materials. NIST 139a and 139b were obtained from the same heat, whereas NIST 139 was extracted from a different heat.

Multistranded Copper Wire. To test the sensitivity of the multivariate LA-ICPMS technique, six individual strands from a
65-strand, high-purity copper wire were analyzed. The trace elements were examined to see whether the individual strands could be differentiated. In this study, seven elements (Table 1) were monitored and nine replicates for each strand were acquired.

To facilitate analysis of the data, we used the modeling approach as opposed to the graphical score plot approach. PCA models were generated for each of the wire strands, and the remaining individual strands were compared to the models. The average $Q$-residual value was calculated for each pair of data sets (Figure 4). As can be seen, each of the six individual strands is distinctly distinguishable from each other even at the 99% confidence level. Conceivably, all 65 strands in the copper wire could be analyzed in a similar manner, and two short segments of this wire could be matched strand by strand to the other, providing a powerful tool for forensic and antiterrorism investigations.

Even more, the PCA process requires precisely the same data (i.e., mass spectra) as would be used for conventional quantitative analysis. To assess this hypothesis, two different metals (brass and NIST 1264a steel) were ablated at different laser focal positions relative to the sample surface. As the laser is defocused, the spot size increases, the power density at the sample surface decreases, and the material sampled and transferred to the plasma becomes less representative of the bulk composition. The resulting mass spectrum can differ from that obtained at a high-power density with the laser focused at the sample surface.

Due to chromatic aberration, the lens focuses the UV laser (266 nm) at a distance above the sample different from the visual image seen through the camera. The optimum focus position of the laser was determined from prior experiments to be the spot where the visual image observed on the camera is defocused by 600–700 μm into the sample. A PCA model was generated from the data acquired near the optimum focus position (denoted as zero in the figures), and the remaining data were compared to this model.

Five elements were monitored in brass, and nine replicates were acquired at each focus position. Figure 5 shows the average $Q$-residual value of the replicates for each focus position for brass.

**Fractionation of Brass and Steel.** We suggest that PCA can also be used with LA-ICPMS to investigate the presence and severity of elemental fractionation for homogeneous solid samples.
tion of the particulates from brass is sensitive to focal position and, thus, to laser fluence or power density. Thus, substantial fractionation occurred as the focus position was changed, as expected for brass.\(^{40}\)

A similar analysis was performed on NIST 1264a steel, which is generally considered to be less susceptible to fractionation than brass.\(^{41}\) These results are shown in Figure 6. For steel, 25 elements were monitored and 9 replicates were acquired at each focus position. The PCA model was generated from data obtained at the optimum focus position (−50, 0, and +50 \(\mu\)m), and the rest of the data were compared to that model. Except for those obtained at the shallowest (first) and deepest (last) focus positions, all of the Q-residual values were below the 95% confidence level and of approximately the same value. Thus, the spectra obtained at most focal positions were not different statistically. We suggest this agreement indicates that little or no fractionation occurred in steel over this range of fluences.

It is important to note that different sample locations are ablated at different fluences, and this procedure for diagnosing fractionation assumes the sample is homogeneous. Variations between measured spectra and the model are attributed to differences in ablation and transport efficiency as the laser fluence is changed, not to actual spatial variation in sample composition. This work was done on highly homogeneous standard reference materials, and nine replicates were measured at each focal condition in order to average out any small variations in analyte concentration at different sampling locations.

**CONCLUSIONS**

The use of PCA with LA-ICP-MS for the forensic matching of solids is efficient, reproducible, and highly selective. The basic methodology developed for the analysis of metals, glasses, and wire can be adapted readily to measure the trace elemental composition of nearly any solid or coating including paints, soils, pharmaceutical materials, gunshot residues, etc. The matching procedure using PCA generates its own quality control (i.e., confidence limits) and does not require subjective judgment as to which elements are most appropriate.

The ability to diagnose and minimize elemental fractionation will strengthen the value of LA-ICP-MS for forensic investigations and improve quantitative capabilities for other applications. In future work, we intend to investigate fractionation effects in materials other than brass, using chemometrics to diagnose the degree of fractionation as a function of both laser power and focusing condition. Ideally, rather than devising a means to correct for fractionation, we hope to identify experimental conditions under which fractionation is minimized or eliminated. One such development involving a femtosecond laser is currently being

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evaluated as a means to significantly reduce matrix dependence and fractionation. It is believed that the shorter pulse length of such a laser generates mechanical ablation rather than melting and splattering. The femtosecond laser pulse is over before the material is ejected, which minimizes effects caused by interactions between the ablated material and the laser beam. The result is more consistent ablation of various elements despite differences in volatility, etc.\textsuperscript{26}

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