Elemental depth profiling of forensic samples by confocal 3D-XRF method

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ABSTRACT
We report the feasibility of discrimination of leather samples related to forensic science by applying confocal 3D-XRF method. The laboratory made confocal 3D-XRF has a spatial resolution of about 14 μm at an energy of 11.4 keV. The characteristic elemental depth profiles and of multilayered leather samples were nondestructively obtained by using confocal 3D-XRF. Elemental depth profiles showed a layered structure obtained at a certain position on the sample. We tried to classify leather samples (natural, synthetic, and artificial) by cluster analysis concerning maximum intensity and maximum depth. The cluster analysis regarding maximum depth and maximum intensity suggested the possibility of discrimination of leather samples.

INTRODUCTION
XRF is a non-destructive analytical method that can be applied to solid or liquid samples. XRF has been widely used to characterize geological and industrial minerals, environmental, archeological, cultural heritage, forensic science etc. (Suzuki, et al., 2006; Berendes, et al., 2006; Sano and Suzuki, 2009; Hatzistavros, et al., 2008; Koons, et al., 1991). In the case of layered forensic samples, elemental depth profiling gives important information for forensic discrimination. For this purpose, the forensic sample is usually angle-polished, and then a cross section of the sample is analyzed by micro analytical methods such as SEM-EDS. However, destructive sample preparation is not suitable for forensic sample, which should be
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kept as evidence for judgment. A recently developed confocal micro-XRF technique combined with polycapillary X-ray lenses enables depth-selective analysis. This method limits the analyzing volume by two X-ray focusing optics attached to the X-ray tube and the detector. The basic principle of confocal 3D-XRF was proposed (Gibson and Kumakhov, 1992). The depth profiling was first demonstrated (Kanngieber, et al., 2003). We have developed a laboratory-made confocal 3D-XRF instrument using small x-ray sources and applied it to plant samples (Tsuji, et al., 2007a; Tsuji and Nakano, 2007b), biological samples (Nakano and Tsuji, 2010), solid/liquid interfaces (Tsuji, et al., 2008), and Japanese handicraft (Nakano and Tsuji, 2009). In addition, our research group recently developed a new confocal 3D-XRF instrument using a high-power fine-focus x-ray source, advanced polycapillary optics, and an SDD with a large sensitive area (Tsuji and Nakano, 2011). The depth resolution of the newly developed 3D-XRF instrument was improved by a factor of 3-4 compared to the resolution of previous 3D-XRF instrument developed in the author’s research group. This new confocal 3D-XRF instrument was applied for analysis of forensic samples such as car paint chips and leather samples, and we found that leather samples have nearly homogeneous layered structure (Nakano, et al., 2011). In this study, to discriminate leather samples related to forensic investigation, depth elemental profiling was performed. In traffic accidents, pieces of leather product (e.g. bag, clothes, etc.) are often left at the scene of the accident. Therefore, pieces of residual leather were measured as forensic sample. Finally, cluster analysis is applied for assigning a set of samples into groups (or clusters) so that the samples with similar characteristics were categorized in the same cluster.

EXPERIMENTAL SETUP
Confocal 3D-XRF system
A new tabletop confocal 3D-XRF system, developed at OCU, was used for the nondestructive depth analysis of forensic samples (Tsuji and Nakano, 2011). A metal ceramic-type 50W x-ray tube with a Mo anode [MCBM 65B-50, rtw, Germany] was operated at 50 kV and 0.6 mA. The focal spot size at the anode of the x-ray tube was 50 μm × 50 μm. Primary x-rays were focused to 10 μm by a polycapillary x-ray full lens attached to the x-ray tube. Another polycapillary half lens was attached to a SDD [Vortex EX-50, SII Nano Technology] (sensitive area: 50 mm², energy resolution <130 eV at 5.9 keV). Each polycapillary lens was designed and manufactured by XOS (East Greenbush, NY) in the USA. The focal spot size of the half lens was experimentally evaluated to be 10 μm at an x-ray energy of 17.4 keV (Mo Kα) by the XOS. Both polycapillary x-ray lenses were set in the optimum confocal geometry
with the angle between the incident and detection beams adjusted to 90˚. The focal spots of both lenses were precisely adjusted to be at one common point by using an X-Y-Z stage. The position of the sample was controlled by stepper motors with a precision of 0.5 μm and driven by a personal computer. The 3D-XRF measurement was performed in air. The depth resolution of the confocal 3D-XRF instrument evaluated by a thin foil scanning method was 14 μm at an energy of 11.4 keV (Tsuji and Nakano, 2011).

**Forensic samples**

Forensic samples were prepared by Forensic Science Laboratory, Hyogo Prefectural Police Headquarters. Three kinds of leather samples (natural, synthetic, and artificial) were analyzed. Table 1 summarizes the information of measured leather samples in this study. The leathers had various colors (black, gray, red, and white). The thicknesses of the leather samples were in the range of 0.5 to 1.3 mm. In the previous work (Nakano, et al., 2011), very simple leather samples with different colors were analyzed by 3D-XRF. In this work, we tried to discriminate the leather samples that had very similar colors.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Color</th>
<th>Data No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthetic</td>
<td>Black (glossy)</td>
<td>1, 1', 1”</td>
</tr>
<tr>
<td>2</td>
<td>Synthetic</td>
<td>Red (glossy)</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Synthetic</td>
<td>Gray</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Synthetic</td>
<td>Dark red</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Synthetic</td>
<td>Black</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Artificial (rough surface)</td>
<td>Black</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Artificial (snake pattern)</td>
<td>Black, White</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>Artificial (snake pattern)</td>
<td>Black</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>Artificial</td>
<td>Gray</td>
<td>9, 9’, 9”</td>
</tr>
<tr>
<td>10</td>
<td>Artificial</td>
<td>Dark Gray</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>Artificial</td>
<td>Black</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>Natural (cow)</td>
<td>Black</td>
<td>12</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

*Elemental depth profiles*
Elemental depth profiles were obtained by scanning the position of the sample in the direction of depth at a fixed position. The results of elemental depth profiles are shown in Fig. 1. In these figures, x axis corresponds to scanned distance in depth direction from the surface (set to zero) into the depth of the leather specimen. It should be emphasized that characteristic elemental information and layered structure were nondestructively obtained. For example, the sample 6 in Fig. 1 (c) showed a layered structure: first layer contains S and Cl, while second layer contains Ca and Ti. Furthermore, it was confirmed that sample 11 in Fig. 1 (f) has a three layered structure. The first, second, and third layer contain Zn, Cl and Ca, respectively. In sample 11, it was suggested that Zn is derived from fire retardant, so Zn is present on surface of the sample.

Depth profiles of samples 4 and 5 in Figs. 1 (a, b), a layered structure was not clearly observed. This would be due to roughness of sample surface and low concentrations of these elements. Additionally, depth profiles of sample 9 and 10 in Figs. 1 (d, e), broad peaks for Zn were observed. This result suggests that Zn was distributed widely from the surface to the inside of material. The elemental depth profiling gives us detailed information on elemental distribution in depth.

![Fig.1 Typical elemental depth profiles of leathers obtained by confocal 3D-XRF. (a) ~ (f) represent sample numbers of 4, 5, 6, 9, 10 and 11 (shown in Table 1), respectively.](image-url)
Cluster analysis

A cluster analysis is useful for assigning a set of data into groups (called cluster) so that the samples with similar characteristics are classified in the same cluster. In this work, the cluster analysis was applied for the forensic leather samples by using OriginPro (version 8.6) software. Twelve leather samples, which are described in Table 1, were classified by using maximum intensity and maximum depth in depth profiles of eight elements (S, Cl, K, Ca, Ti, Cr, Fe, and Zn). Maximum intensity was defined as the highest intensity with each element in depth profile, while maximum depth was defined as the depth of position where the maximum intensity was obtained. As shown in Table 1, (1, 1’, 1”) and (9, 9’, 9”) indicate the data obtained at different positions in the same sample.

The result of classification by maximum depth is shown in Fig. 2 (a). The data numbers of 1, 1’, and 1” (or 9, 9’, and 9”) should be classified in the same group or near group. However, in Fig. 2 (a), these data were not classified in the same group. Almost all leathers are coated with a surface color layer having a similar thickness. Therefore, classification by maximum depth was difficult because maximum depth of each sample showed similar value. If the spatial resolution of the 3D-XRF is improved, more detailed depth information will be obtained and maximum depth will be useful parameter for cluster analysis.

The result of classification by maximum intensity is shown in Fig. 2 (b). Classification between synthetic, artificial, and natural leather was not perfectly successful, however, the data of the same sample (1, 1’, 1” and 9, 9’, 9”) could be classified into near group. Moreover, synthetic leathers (Data No.4&5), which showed similar depth elemental profiles in Fig. 1, were classified into near group, while artificial leathers (Data No.6, 7, 9, 9’, 9”, 10 and 11) were classified into another group as shown in Fig. 2(b). These results indicate that classification by cluster analysis concerning maximum intensity was more effective in grouping than using the maximum depth.

Compared to the intensities of Cl, Ca, and Ti, the intensities of K and Fe were weak. Therefore, these elements may not be useful for cluster analysis. To improve the result of cluster analysis, it would be important to improve the sensitivity of 3D-XRF.
CONCLUSIONS

The nondestructive 3D-XRF method, combined with two individual polycapillary lenses with 10 μm spatial resolution, was demonstrated on multilayered leather samples related to forensic investigation. These multilayered samples have often been analyzed after destructive pretreatment by grinding the surface of the sample to expose each layer for micro-XRF and SEM-EDS. In contrast, confocal 3D-XRF is a powerful tool for the forensic discrimination. It offers a great advantage in 3D elemental analysis that enables depth-selective analysis within a micro region at a specified depth.

The characteristic elemental depth profiles of leather samples were non-destructively obtained by using confocal 3D-XRF. Moreover, cluster analysis by maximum depth and maximum intensity suggested the possibility of discrimination of leather samples.

Analysis for the forensic discrimination requires repeatability and reproducibility of the measurements depending on sample homogeneity. More applications for the actual forensic samples are required so that 3D-XRF analysis can be used as a reliable method.

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