Application of X-Ray Fluorescence Analysis for Forensic Science in Mongolia

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We study the possibility of evaluating the elemental composition of automotive (vehicle) coating paints and determining the gunshot residue from 5.6 mm bullets of a small-caliber gun using the EDXRF technique. An Elvax EDXRF spectrometer, consisting of a Si-PIN detector with a resolution of 200 eV for MnKα radiation with energy of 5.9 keV and a mini X-ray tube with Rh anode, was used. Results of the study showed that the number of shots was directly correlated to the relative intensity of barium and lead on the gunshot target, and the distance of the shooting could be determined using chemical elements intensities, such as Pb, S, Ba and Cu intensities, from the gunshot residue. In the case of automotive paints, the elements identified in the samples were Ca, Ti, Fe, Cu, Cl, Zn, Cr and Pb, and the EDXRF technique could be used for the identification of the different cars by the paint coating samples from the crashed car. This work was the first study which used the EDXRF analysis for automotive paints in Mongolia.

Key words: XRF, application in the forensic science, gunshot residue, automotive paint

In recent years, high sensitivity equipment such as atomic absorption spectroscopy (AAS), total reflection X-ray fluorescence analysis (TXRF) and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX) are being used in forensic examinations to discover and carry out analyses to determine the ele-
mental content and to conduct research on a microscop-
ic trace or invisible traces in dry, liquid or solid materials
at the crime scene. The examples of the materials of in-
terest include soil, sand, biological organs, paint, sur-
rounding soil, water, air, small parts inside the cell and vi-
rus, as well as fiber, clothes, hair, wool, cashmere, sand,
rock and food. These investigations are being made in
order to make a conclusion with a scientific basis by the
requests of law enforcement organizations [1-5]. One of
the analysis methods being used is an energy dispersive
X-ray fluorescence analysis (EDXRF). It is a well-estab-
lished analysis technique for the qualitative and quantita-
tive identification of chemical elements in different sam-
ple, and it allows for accurate, fast, and non-destructive
determination of the elemental composition [6-9].

In Mongolia, the first physics laboratory for the
forensic examination was established in 1978, and an
atomic absorption spectrometry and equipments of in-
frared and ultraviolet light were installed through the
support of the German Democratic Republic. It can
be considered that this has set a basis to develop the
atomic and nuclear techniques for the forensic science
in Mongolia. In 2008, an EDXRF spectrometer from El-
vaTech Ltd (Kiev) was installed at the National Institute
of Forensic Science (NIFS) in Ulaanbaatar, Mongolia.
Nuclear Research Center (NRC) of National Universi-
ty of Mongolia (NUM) and NIFS have cooperated to
develop several methods using the EDXRF spectrom-
etry and to study the possibility of using them for foren-
sic examinations [10-11]. Therefore, it can be said that
these efforts have laid the foundation for determining the
elemental composition of forensic materials using the
XRF analysis.

In the present paper, a development of EDXRF
technique for forensic examinations such as for evalu-
ating the elemental composition of automotive coating
paints and determining the gunshot residue from 5.6
mm bullets of a small caliber gun is described.

EXPERIMENTS AND RESULTS

Apparatus. For the current study, Elvax EDXRF
spectrometer consisting of a Si-PIN detector with ther-
mo-electrical cooling, with a resolution of 200 eV at 5.9
keV, and a mini X-ray tube (5 W power maximum) with
Rh anode and air cooling system was used at the Na-
tional Institute of Forensic Examination, Mongolia.

Study of automotive paints

During the analysis of automotive paints in Mon-
golia, we have studied the possibility of evaluating the
elemental composition of automotive coating paints us-
ing the EDXRF technique. Sliding contact among auto-
mobiles or between an automobile and another surface
commonly produces smears. These chips of paints have
been recognized as an important type of forensic evidence.

Sample Preparation. Samples of 16 main color
paints and coatings were collected from about 20 cars
of different makes. Paints samples were prepared by
smoothly dyeing thin 3x3 cm² size polyester, which
were then dried in ambient conditions for 2 days. And
we directly used paint coatings from cars for the qual-
itative analysis.

In order to determine the elemental content of paints,
ash samples of paints were prepared. We had chosen
two paint samples which were 94.75 g white (code №
075) and 95.55 g red (code № 165) paints. These sam-
ple was burnt at inside burner at 600°C for 4 hours
and then powdered to a particle size of around 70 mi-
cron by the agate pestle. Powder ash samples were pre-
bred by pressing them into dedicatory container with 10
mm thickness, 20 mm diameter and 5 mm Mylar bottom.

Acquisition and Methods. The acquisition time
was 100 s, and XRF spectra were evaluated with the
Elvax software package. The comparison of automotive
paints spectra is shown in Figure 1.

From Figure 1, we can see the dependence of
color of paints on the elemental composition. Further-
more, the pigments in paints may be approximately iden-
tified by their elemental indicators (Table 1) [2]. For ex-
ample, the most common white pigment in use today
is the titanium dioxide, and titanium value in white paint
is the highest among other paints in the above Figure
1. Therefore, the main pigment of white paint (code №
075) may be the “titanium white”.

Comparisons of coating samples from different
white automobiles such as Accent, Kia Bongo and
Nissan, and the white paint sample are shown in Fig-
ure 2. In Figure 2, titanium relative intensities in coat-
ing samples which were collected from the white cars

Table 1

<table>
<thead>
<tr>
<th>Paint Color</th>
<th>Main Element Detected</th>
<th>Pigments (and their identifying elements)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>Ti</td>
<td>Titanium white (Ti)</td>
</tr>
<tr>
<td>Blue</td>
<td>Cu</td>
<td>Copper Phthalocyanine Blue (Cu, possible Cl)</td>
</tr>
<tr>
<td>Yellow</td>
<td>Fe, Zn, Cr</td>
<td>Synthetic red and yellow oxides (Fe), Zinc tetroxycromate (Zn, Cr)</td>
</tr>
<tr>
<td>Red</td>
<td>Cl, Fe</td>
<td>Synthetic red and yellow oxides (Fe), Quinacridone pigments (red, violet, gold) (Cl), Non-metallised Azo Reds (Cl)</td>
</tr>
</tbody>
</table>
have similar values. It was observed that these automobiles were painted by the white paint with titanium dioxide. However, intensity ratios of the Ti/Ca and Ti/Cu have a different variety for each car. It was demonstrated that the EDXRF technique could be used for the identification of different cars by paint coating samples from the crashed car.

**Determination of element content in the automotive paint.** The elemental concentrations in the paint ash were calculated by the following formula [6]:

\[
C_i = I_i \left[ k_i + \sum_j a_{ij} I_j \right] + B_i
\]

where \(k_i\) and \(a_{ij}\) are the correction coefficients, \(B_i\) is the background term. The coefficients were determined by the least-squares fit on the basis of measured reference samples such as SG-2, soil-5, SP-2, SSL-1, SP-3 and other ash references [12, 13]. The correction was done using the intensities rather than the concentrations. The algorithm assumed that the matrix effect of an element \(j\) on the analyte \(i\) is proportional to its intensity. The determination of a single element was possible using this equation.

The results of the calculated elemental contents by formula (1) were compared with chemical analyses in Table 2. Chemical analyses by standard methods were conducted at the Chemistry School of National University of Mongolia and Chemistry and Chemical Technology Institution of Mongolian Science Academy. From Table 2, the results of elemental contents determination by the developed method were fitting with the results of chemical analyses. It showed that the EDXRF technique could be used for the determination of chemical elements contents in the paint ash.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Content in white paint ash (%)</th>
<th>Content in red paint ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1.02 ± 0.16</td>
<td>0.43 ± 0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>0.13 ± 0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0058 ± 0.0007</td>
<td>0.0040</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0018 ± 0.0002</td>
<td>0.28 ± 0.04</td>
</tr>
</tbody>
</table>

**Graphs**

- Figure 2. Comparison of coating samples from different white cars.
- Figure 3. XRF spectrum of a gunshot target.
- Figure 4. Correlation between relative Pb, S and Ba intensity in gunshot targets and the distance of the shooting.

**Study of gunshot residues**

In this part, the possibility of gunshot residue determination from 5.6 mm bullets of small caliber guns, which are widely used in Mongolia, using the EDXRF technique have been studied.

**Sample preparation and measurement.** The samples for 80 bullets with 5.6 mm diameter were collected. First, shooting targets were prepared using the separated 12x12 cm size cotton materials. Prepared targets were then shot by the small caliber gun from different distances including 0 m, 0.5 m, 1 m, 1.5 m and 2 m. Shootings of 1 to 4 times from each distance were done after cleaning the gun hole. After each shot, the study targets were directly measured by Elvax EDXRF spectrometer for the qualitative analysis. Measurement time was 200 s, and their spectrums were evaluated by Elvax software.

**Gunshot residue results.** In order to evaluate the elemental profile of a gunshot residue, we first assured that all the detectable elements that were present could be observed. An XRF spectrum of a gunshot target is shown in Figure 3, which indicated the presence of chemical elements such as Cl, K, Ca, Ti, Cr, Fe, Cu, Zn and Pb in the gunshot target. Correlations of relative intensities of Pb, S and Ba in gunshot targets and distances of the shootings are shown in Figure 4.

Linear correlation of relative intensity of chemical elements and shooting distance is shown in the above figure, and the values of lead and barium are the highest among other chemical elements in the gunshot targets.

Furthermore, Figure 5 demonstrates the dependence of shooting frequency for each distance from the relative intensity of Pb and Ba.
The study of the gunshot residue showed that the number of shootings is directly correlated with relative intensities of barium and lead on the gunshot target, and the distance of the shooting could be determined using several chemical elements intensity in gunshot targets such as Pb, S, and Ba.

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