Chapter 6

Elemental characterization of an antique - ‘A Royal Silver Salver’ using EDXRF technique

6.1 Introduction

Analysis of ancients remains is expected to provide information of the culture, trade, and technology of that time. Many kind of antiques i.e. glasses, coins, paintings, pottery, tiles, paper and inks, and human remains such as femurs and mummy hair etc., are attractive targets of investigation [1-6]. In the western world already all possible analytical tools such as optical and electron microscopy, Carbon-14 dating, Mass spectrometry, and different elemental analysis techniques like Neutron Activation Analysis (NAA), Atomic Absorption Spectroscopy (AAS), X-ray fluorescence induced by charged particle and photons (PIXE, EDXRF, XRD, SYXRF) are being used to study the archeological artifacts [1-4].

Energy dispersive X-ray fluorescence (EDXRF) technique is one of the most suitable analytical method to analyze ancient specimens because of its properties such as non-destructive, multi-elemental, analysis in any physical form of the specimen (solid, liquid, gas), and detection limit up to ppm levels. The present study involves the elemental analysis of the Royal Silver Salver designed by Jahangir’s atelier during his rule in India.

6.2 The Royal Silver Salver

6.2.1 Historical background

Present elemental characterization measurements here are part of a study of the masterpiece in antiquity “A Royal Silver Salver”, most amazing work of highly detailed decorative piece of silver alloy from the Emperor Jahangir’s era, the Mughal period. The antique is taken from personal collection of Mr. Anshul Nagar from Mumbai, India. The Salver is mainly made up of silver metal material used by the Royal Patronage. There was a class of art from ancient times in India which uses hitting, filing and engraving the material (metals and alloys) to make crafts such as statues, grossary and show pieces. Such work is present in many places in India. This royal salver is also one of the great works done by the artists
Fig. 6.1: The face of the Royal Silver Salver. The positions scanned during EDXRF analysis are shown by spots with position number.

during Mughal’s rule in India. Its luster and quality of craftsmanship suggest that it came from families of artists, specialized in a particular medium art or field or technique for the royal patronage over several generations. The Royal patronage of secular art was also a standard feature of Islamic sovereignty that enabled the ruler to demonstrate the splendor of his court and, by extension and the superiority of his state. It also played an important role in the making of the Islamic art, as it has in the arts of other cultures. Mughal art flourished during the late 16th and early 17th centuries with spectacular works of art by master artists such as Ustad Mansur, Basawan, Lal, Miskin, Kesu Das, and Daswanth. This Salver carries with a high resemblance of Ustad Mansur's work, who was a known
naqquash apart from him being well known for paintings and illustration works. Some animals bear similarity to Miskin’s animal illustrations from the realistic and natural species. Som Prakash Verma cited in his book, Mughal painter of Flora and Fauna 'Ustad Mansur' [7] as, “The suffix Naqqash (painter, engraver, sculptor, carver, gilder limner) with Mansur's name in some of the ascriptions on the miniatures would probably suggests that Mansur belonged to a family which was engaged in some sort of a profession as connoted by the word naqqash, or may be had also practiced some form of the art other than painting, which left no record”. Imperial Patronage drew a large number of artist from different regions to the royal studio. Only a few are mentioned in the historical works of that period. All those who came under the royal aegis brought along with them their own
regional traits as well, and helped in evolving a compact, unified and homogeneous form and style of painting, and they could be mostly identified from the ascription given on the miniatures. Such a unified result was achieved through the practice of joint-work in the royal atelier, a system of work that was most ingeniously recommended by Emperor Akbar. This Salver is a masterpiece in itself due to the three dimensional sumptuously engraved formats, which give it depth and enhance its concave low relief work. The concave rhythmic low relief engraving looks to be influenced by Flemish mannerism. Emperor Jahangir was an impassioned collector whose agents traveled far in search of the curious and beautiful creatures. Probably this work seems to be the infusion of techniques and various experiments with material and styles that were carried out in ‘Kitabkhana’ of Emperor Jahangir, by the master artist. The engraving hatching and linning on the relief works is also correlating the engraving done by Albrecht Dürer (15th-16th century).

6.2.2 Physical appearance of silver Salver

The royal silver salver is circular in shape. It has variety of art. The work is smartly distinguished by dividing in different portions. Four concentric circles confine the different portions. Each circle has different arc thickness (Fig.6.1). These are as follow:

(i) The inner most circle: It has stylized Peacock inside which is named as Hamsa. The diameter of the circle is nearly 4.65 cm and the arc is 2 mm thick.

(ii) Second circle: its diameter is nearly 8.45 cm and thickness of its arc is 4.5 mm. The region between innermost and this circle has Sacred Kalma written inside it.

(iii) Third circle: Its diameter is 12.5 cm and thickness of its arc is 5 mm almost uniformly. In the region between second and third circle flowers are shown by engraving metal.

(iv) Fourth circle: Its diameter is 35 cm almost in every direction and thickness of its circular boundary is almost in every direction is 2.5 mm. The region between third and fourth circle has largest area in which various animals, birds and creatures of nature are shown by the artist. In this region, also there is a mysterious bird shown which is named as Simurgh. This Simurgh has two eyes shown, one on its place in body and other on the neck. In this bird the historians found the signature of the artist Mansur. So, this salver is supposed to be made by the famous naqqash of the Mughal times Ustad Mansur.

The region outside the fourth circle up to edge is molded upwards to give a finish by the artist. The planner thickness of the salver lies in 2.1 to 2.4 mm due to the craft work
performed on its surface. From edge to edge, the diameter is 41.9 cm. The weight of the salver is 2.49 kg.

6.3 Experimental procedure

The elemental composition of the royal silver salver is deduced using radioisotope based energy dispersive X-ray fluorescence technique. The reflection mode geometrical system used for these measurements has shown in Fig. 6.3.

![Reflection mode geometrical system](image)

Fig. 6.3: (a) Reflection mode geometrical set-up used in present measurements (b) picture of the experimental set up during measurements.

The geometrical set up involved $^{241}$Am radioisotope source as photon source. The photon source was made quasi monochromatic to obtain 59.54 keV $\gamma$-ray using a copper and aluminium successive absorbers for 26.2 keV $\gamma$-ray and Np L X-rays. An LEGe detector in horizontal configuration ($100 \text{ mm}^2 \times 10 \text{ mm}$, 8-$\mu$m Be window and FWHM = 150 eV at 5.895 keV, Canberra, US) in the horizontal configuration coupled with PC based multichannel analyzer (Multiport II) has been used to collect the X-ray fluorescence spectra from the samples through Pb collimator. A cylindrical thick Pb shielding is prepared for shielding the detector from unwanted photons from environment. Salver is a single piece of metal alloy which is crafted by engraving the alloy surface and given various shapes on the surface e.g. the animals, birds, plants and flowers. Because of its engraved surface it was expected to have variation in metal compositions throughout the surface. The elemental analysis was performed at different spots of the surface of the salver. The region visible to the detector was identified by using a Zn disc on the target (spot on the salver). A laser
Fig. 6.4: Pictures for various spots given along with their names.
fixed on the detector shield with beam spot on the Zn disc. The Zn disc was removed and the spot on the salver under the beam spot was used as the target spot. The different animals and birds crafted over the salver surface in outer region were emphasized to analyze. Different spots selected on the salver were marked as shown in Fig. 6.1 and are given with their names in Fig. 6.4-6.5. Typical spectra for the front surface and back surface are shown in Fig. 6.6.

### 6.4 Evaluation Procedure

The EDXRF spectra recorded for front and back side surface of the royal silver salver is shown in Fig. 6.6. The spectra have characteristic X-ray peaks of elements present in the specimen, escape peaks, and Rayleigh and Compton scatter peaks for incident 59.54 keV γ-rays. The peak area of characteristic X-rays is used to determine the concentration of corresponding element.
Fig. 6.6: (a) Typical full range X-ray fluorescence spectra for the front and back surfaces of the salver. (b) Expanded view of the spectra marked in square in full spectra containing L X-rays for Hg. In expanded view the Y axis scale is set to linear.
The escape peaks in the spectra are additional peaks due to Ge detector crystal. In Ge detector, escape peaks occur if the energy of incident photon is above the \( K \) edge energy of Ge (\( E_K = 11.104 \text{ keV} \)), it can generate characteristic X-rays from the Ge crystal. The energy deposited is less if these x-rays escape the detector active volume. For each such photon of energy \( E_{ph} \) (in keV), two escape peaks are possible at energies

\[ E_{esc\alpha} = E_{ph} - 9.876 \text{ keV}, \text{ and } E_{esc\beta} = E_{ph} - 10.983 \text{ keV}; \]

where the 9.876 keV and 10.983 keV are the average energies of the \( K\alpha \) and \( K\beta \) X-rays of Ge, respectively. In Ge detector, the escape probability is highest for lines close to the Ge \( K \) absorption edge at 11.104 keV. For normal incidence of photon and neglecting escape through the sides and rear of the detector, the ratio of the number of counts in the \( K \) escape peak, \( N_e \), to the number of counts in the full-energy peak, \( N (= N_e + N_p) \), gives the escape probability by

\[
\frac{N_e}{N} = 0.5 \omega_K \left[ 1 - \frac{1}{r} \right] \left[ 1 - \frac{\mu(E_K)}{\mu(E)} \ln \left( 1 + \frac{\mu(E)}{\mu(E_K)} \right) \right]
\]

(6.1)

where \( E \) is the energy of incident photons, \( E_K \) is the mean energy of Ge \( K \) x-rays, \( \omega_K \) is the fluorescence yield (\( \omega_K = 0.535 \)), \( r \) is the Ge attenuation coefficient just above and below the \( K \) edge (\( r = 7.011 \)), \( \mu \) is the Ge attenuation coefficient at \( E \) or \( E_K \). The escape peak probability corresponding to the Ge \( L \) x-rays is low \(< 1 \% \) because of low energy and low fluorescence yield value.

The area of the characteristic X-ray peak not interfering with the other X-ray peaks has been used for the calculation of elemental concentration. From the spectra in Fig. 6.7(a) peak area of \( K\alpha \) X-ray peaks of Ag and Cd are used for elemental analysis. Hg is quantified by using the peak area of \( L\alpha \) X-ray peak (Fig. 6.7 (b)). Fundamental parameter approach was used to determine the elemental concentrations in the alloy salver. The observed count rate \( (N_i) \) for a characteristic X-ray of \( i \)th element is related to the corresponding elemental concentration \( (m_i) \) in the target sample and intensity of the exciting radiation \( (I_o) \) as

\[
N_i = I_o G E_i m_i \beta_i \sigma_i
\]

(6.2)

where \( G \) is the geometrical factor, \( \varepsilon_i \) is the detector efficiency at the X-ray energy, and \( \sigma_i \) is the X-ray fluorescence cross section, and \( \beta_i \) is the absorption correction factor that accounts for absorption of the incident and emitted X-rays in the sample. The details of the
expression for $\beta$ and its evaluation are discussed in chapter 2. The expression for the absorption correction factor ($\beta$) in the reflection geometrical set-up is given by

$$
\beta = \frac{1 - \exp \left[ - \sum_i \left( \frac{\mu_i}{\cos \theta_1} + \frac{\mu_2}{\cos \theta_2} \right) m_i \right]}{\sum_i \left( \frac{\mu_i}{\cos \theta_1} + \frac{\mu_2}{\cos \theta_2} \right) m_i}
$$

(6.3)

where summation over $i$ stands for different elements present in the compound target. $\mu_i$, $\mu_2$ are the mass attenuation coefficients (cm$^2$/g) corresponding to the incident and emitted photon energies, respectively, in the $i$th element and were taken from the tables of Storm and Israel [7]. $m$ is the thickness of the target in g/cm$^2$. $\theta_1$ and $\theta_2$ are the angle made by the incident and the emitted photons with normal to the target surface, respectively. In present calculations, the expression for absorption correction factor ($\beta$) taking into account the values of $\theta_1$ and $\theta_2$ to be 45° and 0°, respectively, can be given by

$$
\beta = \frac{1 - \exp \left[ - \sum_i \left( \sqrt{2} \mu_i + \mu_2 \right) m_i \right]}{\sum_i \left( \sqrt{2} \mu_i + \mu_2 \right) m_i}
$$

(6.4)

The targets having thickness more than a value that can provide 99% of the maximum count rate for the emitted fluorescent X-rays are taken as infinitely thick targets. A value of $\beta$ equal to 0.21 corresponds to 99% attenuation and below this value of $\beta$, the product $m\beta$ can be safely taken as constant, equal to $\left( \sqrt{2} \mu_i + \mu_2 \right)^{-1}$. Infinitely Thick $^{47}$Ag and $^{48}$Cd foils are excited as standard targets. For $^{80}$Hg element thick standard target was prepared by packing $^{80}$Hg liquid in a perspex ring covering both sides by mylar film. The measurements were performed using the standard targets in the same geometrical set up by replacing the specimen. A straightforward method to obtain the net area of an isolated peak in a spectrum was used, which involves subtraction of the background counts linearly interpolated from above and below the peak from the total counts observed in the peak region. The multichannel analyzer in the set up gives the spectrum in the CNF (binary format with header) format which is converted to ASCII format and the peak area calculations were performed using windows-based software Quattro-Pro. Using the count rate ($N$) from the standard target of an element, the X-ray production cross section ($\sigma$) at the incident energy, i.e., 59.54 keV, taking mass of the target 1 g/cm$^2$ as infinitely thick,
and self-absorption correction factor for incident and emitted energy photons, the \( I_0 G \varepsilon \)
factor is calculated using relation 6.2.

In case of the unknown target, where the thickness is of the order of micrograms usually
absorption factor approach to one means attenuation becomes very less, it become easier to
find the composition using direct unitary method using thin standard target of the thickness
of the same order. Here, in the case of thick metal alloy plate, it was necessary to define the
matrix for the self-absorption for the incident and emitted X-rays of elements present in
salver. For the quantitative elemental analysis, the iteration method is used. In the first step,
the count rate under the characteristic X-ray peaks observed in the spectrum corresponding
to the identified elements was used in the Eq. (6.2) for first estimation of mass
concentration \( m_i \) of the various identified elements. For first estimation a value of \( \beta = 1 \)
has been used to deduce the concentration values. In second step, taking the deduced
composition of Ag-Cd alloy in first step, next estimation of mass concentrations were
determined using new values of \( \beta \) calculated for this composition. This step was repeated
few times after absorption correction using new values of \( \beta \) to get converging values to be
mass concentrations of various elements.

Main metals constituting the alloy are Ag and Cd. This alloy is used by artist to make the
peace of art. It is observed from the analysis that a thin layer silver amalgam is present on
the engraved surface of the silver salver, because of the presence of mercury on the front
surface of it. The function of this amalgam coated on the piece of art is to reserve this piece
and not top get rusted by the environmental cautions. To increase its life and preserve its
shine, polishing by amalgam was used generally at the old times.

To determine the Ag content combined with Hg forming amalgam here back calculation is
used instead of iteration method. In first step effective thickness for standard target of
mercury is calculated, and using the count rate of Hg element from the layer \( (N_{tgt}) \) and the
standard target \( (N_{std}) \), effective thickness for the Hg element on layer \( (m\beta)_{tgt} \) is obtained
using equation

\[
\frac{N_{std}}{(m\beta)_{std}} = \frac{N_{tgt}}{(m\beta)_{tgt}}
\]

(6.5)

Knowing the value of the \( (m\beta)_{tgt} \) thickness of the amalgam is back calculated by varying
mass in the \( (m\beta)_{tgt} \) calculation for the layer using Eq. 6.2 until the calculated value match
with the value obtained using Eq. 6.3.
Table 6.1: Metal composition and concentration of silver and mercury in amalgam coated on different places on salver surface.

<table>
<thead>
<tr>
<th>Spots no.</th>
<th>Name of the spot</th>
<th>Ag Cd Alloy composition (%)</th>
<th>Ag-Hg amalgam Concentration both elements (mg/cm²)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>1</td>
<td>Stylized Peacock (Hamsa)</td>
<td>87.11</td>
<td>12.89</td>
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<tr>
<td>2</td>
<td>Stylized Peacock (Hamsa)</td>
<td>87.02</td>
<td>12.98</td>
</tr>
<tr>
<td>3</td>
<td>Kalma</td>
<td>86.98</td>
<td>13.02</td>
</tr>
<tr>
<td>4</td>
<td>Kalma</td>
<td>87.06</td>
<td>12.94</td>
</tr>
<tr>
<td>5</td>
<td>Kalma</td>
<td>87.08</td>
<td>12.92</td>
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<tr>
<td>6</td>
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<tr>
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<td>Flowers</td>
<td>87.08</td>
<td>12.92</td>
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<td>Flowers</td>
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</tr>
<tr>
<td>10</td>
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</tr>
<tr>
<td>11</td>
<td>Elephant 2</td>
<td>87.47</td>
<td>12.53</td>
</tr>
<tr>
<td>12</td>
<td>Heron and Parrot combat</td>
<td>87.27</td>
<td>12.73</td>
</tr>
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<td>13</td>
<td>Dog</td>
<td>86.39</td>
<td>13.61</td>
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<td>14</td>
<td>Lioness</td>
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<td>15</td>
<td>Simurgh combat</td>
<td>86.31</td>
<td>13.69</td>
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<td>Simurgh combat</td>
<td>86.31</td>
<td>13.69</td>
</tr>
<tr>
<td>17</td>
<td>Phoenix</td>
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<tr>
<td>18</td>
<td>Lion hunts a rabbit</td>
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<td>12.55</td>
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<td>Running Deer</td>
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<td>86.94</td>
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Results and discussions

The energy dispersive X-ray fluorescence (EDXRF) technique is used to find the alloy composition and the materials used in finishing of the royal silver salver. The salver was marked at 30 spots in its five major portions to check the uniformity of composition. From the analysis it appears that main metals constituting the alloy are Silver (Ag) and Cadmium (Cd). The alloy composition is almost same throughout the salver surface and found to be 87% Silver (Ag) and 13% of cadmium (Cd).

During analysis there were indications of presence of mercury (Hg) in case of front surface which indicates that there is possibly a thin layer of mercury amalgam on the front surface. The function of this amalgam coat on the piece of art is to preserve this piece and not to get tarnished due to the environmental exposures.

At the ancient times, this amalgam technique was used for preserving the shine for longer periods for such specimen. Also, the concentration values for mercury in the amalgam layer are found to vary significantly (estimated range ~ 1 - 6 mg/cm²). This variation indicates possibility of either the formation of non uniform layer of amalgam at the time of finishing or destruction of the upper layer coating during cleaning over a long period. From the analysis it is concluded that main elements constituting the alloy are Ag and Cd. P. Dasgupta and A. Dutta [9] investigated the silver coins of Mughal times and reported the presence of Ag and Cd. Similar kind of alloy is used for the salver. The presence of $^{117}$Ag
and $^{48}\text{Cd}$ supports the possibility of Silver salver to be belonging to early Mughal times, \textit{i.e.}, 16 to 17\textsuperscript{th} century.

### 6.6 Summary

EDXRF technique is used for the elemental analaysis of a masterpiece ‘A Royal Salver’. The salver is found to be made of an alloy of $^{47}\text{Ag}$ and $^{48}\text{Cd}$ metals with percentage composition 87\% and 13\%, respectively. The front grooved surface of the salver is having a silver amalgam layer on it, to avoid tarnishing of silver. The concentration for mercury in the amalgam layer is found non uniform. EDXRF technique is useful in analysis of the antiques and can be helpful in finding the age of the specimen on the basis of its composition. The composition can be used by comparing it to the available literature for the composition of specimen of particular time. Royal salver is found to be made up in early mughal times \textit{i.e}, 16 to 17\textsuperscript{th} century.
References
