**Determination of Gold in Gold Jewelry Alloys by a Synthesis Method**

Hui Li, Fei DUAN, Xuan WANG, Yong ZHU and Ying-kun GONG  
Chongqing Academy of Metrology and Quality Inspection, Chongqing 401123, China

**Keywords**: Gold jewelry, EDXRF, Density, Nondestructive, Determination.

**Abstract.** Nondestructive determination of Au in gold ornaments mainly takes density method and X ray fluorescence spectrometer with energy dispersion (EDXRF), which exist disadvantages. This paper based on the principle of crystallography, deduced the mathematical relationship between the crystallographic parameters, the density and the impurities content in gold jewelry alloys, then introduced the results by density testing and determination of Ag and Cu by EDXRF into the mathematical relationship, and obtained the gold weight percent in gold jewelry alloys. The results show that obtained the gold weight percent and determination of Au by fire assay are almost consistent, which the error is less than 0.12 %, so establishes a synthesis method of determination of Au by EDXRF and density testing, solves the disadvantages which EDXRF only detects on gold jewelry surface and small area, and density testing cannot detect gold jewelry alloy and demands that jewelry shape is simple, and provides an effective synthesis way for determination of Au in gold jewelry alloys.

**Introduction**

In these years, scholars have carried on a lot of research on quantitative precious metal in precious metal materials and jewelry, which involved mainly density method, X ray fluorescence spectrometry (XRF), X ray fluorescence spectrometer with energy dispersion (EDXRF), scanning electron microscopy and energy spectrometer (SEM-EDXRF), electron probe spectroscopy (EMP-EDXRF), fire assay, induced-coupled plasma-atomic emission spectrometry (ICP-AES), and flame atomic absorption spectrometry (FAAS) etc. These methods have disadvantages that density testing cannot detect gold jewelry alloy and demands that jewelry shape is simple. XRF, EDXRF, SEM-EDXRF and EMP-EDXRF are poor in penetration depth, and can only test on sample surface and small area, and fire assay, ICP-AES and FAAS are destructive test. Therefore, it is necessary to develop a more scientific nondestructive method for determination of Au in gold jewelry alloys. This paper based on the principle of crystallography, deduced the mathematical relationship between the density, the crystallographic parameters and the impurities content in gold jewelry alloys, established a synthesis method of determination of Au by EDXRF and density testing, so solving the disadvantages of EDXRF and density testing, which the reliability was verified by fire assay, and providing an effective synthesis way for determination of Au in gold jewelry alloys.

**Experiments**

**Materials and Specimens**

The information and the photo of gold jewelry samples are shown in Table 1 and Figure 1, respectively.

<table>
<thead>
<tr>
<th>No</th>
<th>Name</th>
<th>Quality(g)</th>
<th>No</th>
<th>Name</th>
<th>Quality(g)</th>
<th>No</th>
<th>Name</th>
<th>Quality(g)</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>3.976</td>
<td>3</td>
<td>Bracelet</td>
<td>13.269</td>
<td>5</td>
<td>Necklace</td>
<td>10.239</td>
</tr>
<tr>
<td>2</td>
<td>Necklace</td>
<td>7.639</td>
<td>4</td>
<td>Necklace</td>
<td>12.649</td>
<td>6</td>
<td>Bracelet</td>
<td>10.586</td>
</tr>
</tbody>
</table>
Instruments and Apparatus

![Image of jewelry samples](image)

Figure 1. The photo of the gold jewelry samples.

The EDXRF consisted of a Rh-anode side window low power X-ray tube (50W, 50kV, 2mA, 125 µm Be window), a Si(Li) detector with 150eV FWHM at MnKα, and the range of analysis elements and determination of element content are from $^{11}$Na to $^{92}$U and from ppm to 100 %, respectively. Density testing system mainly consisted of the electronic balance with 0.1mg precision, the vacuum system and the hanging wire for weighting sample in water etc. Instruments for fire assay mainly consisted of the cupellation furnace with temperature up to 1300°C and temperature difference less than 20°C, the small sheet mill rolling with thickness of not more than 0.1mm, and the analysis balance with 0.01mg precision etc.

Principle and Model

Because gold unit cell is face centered cubic (F.C.C.) crystal structure which consist of 4 gold atoms, the quality of a gold unit cell is 4 gold atomic weight, and the unit cell volume is $a_p^3$ ($a_p$ is the lattice constant of gold unit cell), then the volume of 1 molar gold atoms occupying is $N_0 a_p^3/4$, and gold density can be obtained by the following Eq. 1.

$$\rho_x = \frac{M}{V} = \frac{m_p}{N_0 a_p^3/4} = \frac{4m_p}{N_0 a_p^3}$$

(1)

There $M$ is gold atoms weight in gold unit cell, $V$ is gold unit cell volume, $N_0$ is the A Fugadero constant ($6.022 \times 10^{23}$/mol), $m_p$ is gold molar atomic weight (g/mol). The molar atomic weight of gold, silver and copper is 196.96, 107.868 and 63.5, respectively.

Due to gold, silver, and copper are F.C.C crystal structure, silver and copper atoms replaced respectively gold atoms and formed gold solid solution with F.C.C. crystal structure which changed lattice constant and quality. The Eq. 1 explain if known density, corrected lattice constants, quality, and silver and copper content soluble in gold solid solution, can obtain the gold content in gold solid solution (gold alloy).

Results and Discussion

Determination of Density

Based on Archimedes's law, the sample density is determined by the following Eq. 2.

$$\rho_s = \frac{m}{m_1 + m_2}$$

(2)

The data on the samples by density testing are shown in Table 2.

<table>
<thead>
<tr>
<th>No</th>
<th>$m$</th>
<th>$T$</th>
<th>$\rho_1$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$\rho_x$</th>
<th>$N_0$</th>
<th>$m$</th>
<th>$T$</th>
<th>$\rho_1$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$\rho_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.976</td>
<td>15.7</td>
<td>0.99901</td>
<td>3.812</td>
<td>0.042</td>
<td>19.28</td>
<td>4</td>
<td>12.64</td>
<td>16.</td>
<td>0.99893</td>
<td>12.02</td>
<td>0.043</td>
<td>18.94</td>
</tr>
<tr>
<td>2</td>
<td>7.639</td>
<td>16.0</td>
<td>0.99897</td>
<td>7.284</td>
<td>0.042</td>
<td>19.22</td>
<td>5</td>
<td>10.23</td>
<td>17.</td>
<td>0.99880</td>
<td>9.731</td>
<td>0.042</td>
<td>18.59</td>
</tr>
<tr>
<td>3</td>
<td>13.26</td>
<td>15.8</td>
<td>0.99900</td>
<td>12.61</td>
<td>0.041</td>
<td>19.12</td>
<td>6</td>
<td>10.58</td>
<td>14.</td>
<td>0.99918</td>
<td>10.03</td>
<td>0.042</td>
<td>17.89</td>
</tr>
</tbody>
</table>
There $T$ is experiment temperature($^\circ$C), $\rho_s$ is sample density at $T$ $^\circ$C (g/cm$^3$), $m$ is sample weight in air (g), $m_1$ is the weight of specimen placed on hanging wire in water (g), $m_2$ is hanging wire weight in water (g), $\rho_1$ is water density at $T$ $^\circ$C (g/cm$^3$).

**Determination of Impurities**

Determination of impurities in the samples by EDRXF are shown in Table 3.

<table>
<thead>
<tr>
<th>N</th>
<th>Cu(%)</th>
<th>Ag(%)</th>
<th>$a \times 10^{-8}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.10</td>
<td>4.076</td>
</tr>
<tr>
<td>2</td>
<td>0.00</td>
<td>0.40</td>
<td>4.076</td>
</tr>
<tr>
<td>3</td>
<td>0.51</td>
<td>0.51</td>
<td>4.069</td>
</tr>
</tbody>
</table>

Based on Vegard low\[12\], the solid solution formed by components of same crystal structure is of a linear relationship as Eq. 3 between the lattice parameters and the components content. Because the lattice constant of gold unit cell (4.076×10$^{-8}$ cm) and the one of silver (4.086×10$^{-8}$ cm) is almost the same, regardless of silver atom displacement gold atom effected on the lattice constant, and only involved effect for copper(3.615×10$^{-8}$ cm).

$$a_s = x_1a_1 + x_2a_2 \quad (3)$$

There $a_s$, $a_1$ and $a_2$ are respectively the lattice constant of gold solid solution (gold jewelry alloy) and the one of gold and copper. $x_1$ and $x_2$ are respectively the atom percent of gold and silver and the one of copper in gold jewelry alloy. Intrduced determination of gold, silver and copper atom percent by EDXRF into Eq. 3, and lattice constant $a_s$ for the samples are shown in Table 3.

The quality of gold solid solution can be obtained by the following Eq. 4.

$$m = m_p \cdot x_p + \sum_{i=1}^{n-1} m_i \cdot x_i \quad (4)$$

There $m$ is the quality of gold solid solution, $m_p$ is gold molar atomic weight, $x_p$ is gold atom percent, $m_i$ is impurity $i$ molar atomic weight, $x_i$ is impurity $i$ atom percent.

Intrduced Eq. 4 into Eq. 1 and converted to Eq. 5. There $\rho_s$ is the density of gold solid solution (gold jewelry alloy), $N_o$ is the A Fugadero constant (6.022 × 10$^{23}$/mol),

$$\rho_s = \frac{m_p \cdot x_p + \sum_{i=1}^{n-1} m_i \cdot x_i}{\frac{1}{4} N_o \cdot a_s \cdot \rho_s} \quad (5)$$

$$m_p \cdot x_p + \sum_{i=1}^{n-1} m_i \cdot x_i = \frac{1}{4} N_o \cdot a_s \cdot \rho_s \quad (6)$$

$$x_p = \frac{\frac{1}{4} N_o \cdot a_s \cdot \rho_s \cdot \sum_{i=1}^{n-1} m_i \cdot x_i}{m_p} \quad (7)$$

Impurity $i$ atom percent can be obtained by the following Eq. 8. There $w_i$ is impurity $i$ weight percent, $w_p$ is gold weight percent.
\[
x_i = \frac{\frac{w_i}{m_i}}{\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p}} \quad (8)
\]

Introduced Eq. 8 into Eq. 7 and converted to Eq. 9.

\[
x_p = \frac{1}{4} N_o a_x^3 \rho_x \sum_{i=1}^{n-1} \frac{w_i}{(\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p})} \quad (9)
\]

Gold weight percent can be obtained by the following Eq. 10.

\[
w_p = \frac{m_p \cdot x_p}{m_p \cdot x_p + \sum_{i=1}^{n-1} m_i \cdot x_i} \quad (10)
\]

Introduced Eq. 6 into Eq. 10 and converted to Eq. 11.

\[
w_p = \frac{m_p \cdot x_p}{\frac{1}{4} N_o a_x^3 \rho_x} \quad (11)
\]

Introduced Eq. 9 into Eq. 11 and converted to Eq. 12.

\[
w_p = \frac{\frac{1}{4} N_o a_x^3 \rho_x \sum_{i=1}^{n-1} \frac{w_i}{(\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p})}}{\frac{1}{4} N_o a_x^3 \rho_x} = 1 - \frac{\sum_{i=1}^{n-1} \frac{w_i}{m_i \cdot x_i}}{\frac{1}{4} N_o a_x^3 \rho_x} \quad (12)
\]

Gold weight percent may also be obtained by the following Eq. 13

\[
w_p = 1 - \sum_{i=1}^{n-1} w_i \quad (13)
\]

Introduced Eq. 13 into Eq. 12 and converted to Eq. 14.

\[
\sum_{i=1}^{n-1} w_i = \frac{\sum_{i=1}^{n-1} \frac{w_i}{(\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p})}}{\frac{1}{4} N_o a_x^3 \rho_x}
\]

\[
\frac{1}{4} N_o a_x^3 \rho_x \sum_{i=1}^{n-1} w_i = \sum_{i=1}^{n-1} \frac{w_i}{(\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p})}
\]
\[
\frac{1}{\pi} N_o \cdot a^3 \cdot \rho_x = \frac{1}{\left( \sum_{i=1}^{n-1} \frac{w_i}{m_i} \right) + \frac{w_p}{m_p}}
\]

\[
\frac{w_p}{m_p} = \frac{1}{\frac{1}{\pi} N_o \cdot a^3 \cdot \rho_x} - \frac{\sum_{i=1}^{n-1} w_i}{m_i}
\]

\[
w_p = \frac{4m_p}{N_o \cdot a^3 \cdot \rho_x} - m_p \sum_{i=1}^{n-1} \frac{w_i}{m_i}
\]

(14)

Introduced the results by density testing (shown in Table 2), determination of Ag and Cu by EDRXF (shown in Table 3) and corrected \(a_x\) (shown in Table 3) into Eq. 14, and gold weight percent for the samples are shown in Table 4.

<table>
<thead>
<tr>
<th>No</th>
<th>(w_p(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.97</td>
</tr>
<tr>
<td>2</td>
<td>99.70</td>
</tr>
<tr>
<td>3</td>
<td>99.00</td>
</tr>
<tr>
<td>4</td>
<td>98.13</td>
</tr>
<tr>
<td>5</td>
<td>96.13</td>
</tr>
<tr>
<td>6</td>
<td>91.86</td>
</tr>
</tbody>
</table>

Table 4. The gold weight percent obtained by Eq. 14.

**Determination of Gold by Cupellation Method**

Added appropriate silver to the specimen, and sealed with lead foil, cupellation furnace was heated to 920°C, so the oxidation of lead and impurities leaved gold and silver in the specimen, separated the gold and silver in the cupel by nitric acid, and then weighted and obtained gold weight percent by the following Eq. 15, at the same time, which was compared with standard gold specimen, so eliminated the error in analysis process.

\[W_{Au} = \frac{m_1 + \Delta m}{m_1} \times 100\]

(15)

\(W_{Au}\) is gold weight percent for the samples, \(m_1\) is sample quality (mg), \(m_2\) is the gold quality of separated impurities in specimen (mg), \(\Delta m = m_3 \times E - m_4\) (mg). \(m_3\) is the quality of standard gold specimen (mg), \(m_4\) is the standard gold specimen quality of separated impurities (mg), \(E\) is the purity of standard gold specimen (%).

Determination of Au by fire assay are shown in Table 5.

<table>
<thead>
<tr>
<th>No</th>
<th>(m) (mg)</th>
<th>(m_2) (mg)</th>
<th>(m_3) (mg)</th>
<th>(m_4) (mg)</th>
<th>(E(%))</th>
<th>(\Delta m = m_3 \times E - m_4) (mg)</th>
<th>(W_{Au}(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>202.88</td>
<td>202.97</td>
<td>301.66</td>
<td>301.88</td>
<td>99.99</td>
<td>-0.25</td>
<td>99.92</td>
</tr>
<tr>
<td>2</td>
<td>245.72</td>
<td>245.12</td>
<td>309.65</td>
<td>309.96</td>
<td>99.99</td>
<td>-0.34</td>
<td>99.62</td>
</tr>
<tr>
<td>3</td>
<td>268.16</td>
<td>265.59</td>
<td>272.91</td>
<td>273.21</td>
<td>99.99</td>
<td>-0.33</td>
<td>98.92</td>
</tr>
<tr>
<td>4</td>
<td>280.42</td>
<td>275.31</td>
<td>265.96</td>
<td>266.32</td>
<td>99.99</td>
<td>-0.39</td>
<td>98.04</td>
</tr>
<tr>
<td>5</td>
<td>259.13</td>
<td>249.25</td>
<td>267.12</td>
<td>267.50</td>
<td>99.99</td>
<td>-0.41</td>
<td>96.03</td>
</tr>
<tr>
<td>6</td>
<td>326.67</td>
<td>300.12</td>
<td>300.58</td>
<td>300.98</td>
<td>99.99</td>
<td>-0.43</td>
<td>91.74</td>
</tr>
</tbody>
</table>

Table 5. The data on the samples by cupellation method.

**Discussion**

Determination of Au in gold jewelry alloys by fire assay is a standard method recognized in the world\[13\], it is suitable for determination of 37.50 % - 99.95 % Au in gold jewelry alloys, which the error is less than 0.03 %, and is used usually as arbitration test. Known from Table 6, the gold weight percent (\(w_p\)) obtained by Eq. 14 and determination of gold (\(W_{Au}\)) by fire assay are almost consistent, which \(w_p - W_{Au}\) is less than 0.12 %, so verified the reliability of results by Eq.14, and the synthesis way for determination of Au in gold jewelry alloys is effective and reliability.
Table 6. The data by EDXRF, density testing, fire assay and Eq. 14.

<table>
<thead>
<tr>
<th>No</th>
<th>Name</th>
<th>( m (\text{g}) )</th>
<th>( \rho_x (\text{g/cm}^3) )</th>
<th>Ag(%)</th>
<th>Cu(%)</th>
<th>( a_x \times 10^8 \text{ cm} )</th>
<th>( w_p )</th>
<th>Cupellation ( w_{Au} ) (%)</th>
<th>( w_p - w_{Au} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pendant</td>
<td>3.976</td>
<td>19.282</td>
<td>0.10</td>
<td>0.00</td>
<td>4.076</td>
<td>99.97</td>
<td>99.92</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>Necklace</td>
<td>7.639</td>
<td>19.222</td>
<td>0.40</td>
<td>0.00</td>
<td>4.076</td>
<td>99.70</td>
<td>99.62</td>
<td>0.08</td>
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<td>Necklace</td>
<td>13.269</td>
<td>19.128</td>
<td>0.51</td>
<td>0.51</td>
<td>4.069</td>
<td>99.00</td>
<td>98.92</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
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<td>12.649</td>
<td>18.944</td>
<td>1.00</td>
<td>1.00</td>
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<td>98.13</td>
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<td>10.239</td>
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<td>4.048</td>
<td>96.13</td>
<td>96.03</td>
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</tr>
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<td>6</td>
<td>Bracelet</td>
<td>10.586</td>
<td>18.979</td>
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<td>4.30</td>
<td>4.020</td>
<td>91.86</td>
<td>91.74</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Conclusion

1) Due to gold, sliver, and copper are F.C.C crystal structure, sliver and copper atoms replaced respectively gold atoms and formed gold solid solution (gold jewelry alloy) with F.C.C.crystal structure which changed lattice parameters and quality. Based on the principle of crystallography, established the following mathematical relationship between the crystallographic parameter, density and impurities content in gold jewelry alloys.

\[
 w_p = \frac{4m_p}{N_o \cdot a^3 \cdot \rho_x} - m_p \sum_{i=1}^{n-1} \frac{w_i}{m_i} 
\]

(14)

2) Introduced the results by density testing, determination of Ag and Cu by EDXRF and corrected \( a_x \) in gold jewelry alloys into Eq. 14, can accurately obtain the gold weight percent (\( w_p \)), which is almost consistent with determination of Au by cupellation method, and \( w_p - w_{Au} \) is less than 0.12 %. Thus, this method establishes a comprehensive method of determination of Au by EDXRF and density testing, and solve the disadvantages that EDXRF only detects on the gold jewelry surface and a small area, and density testing demands that the jewelry shape is simple and cannot detect gold jewelry alloys, and provides an effective synthesis way for determination of Au in gold jewelry alloys.

References


