

# Rapid synthesis determination of gold in gold jewelry alloys

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**Keywords:** gold jewelry, EDXRF, density, nondestructive determination, rapid

**Abstract.** The nondestructive determination of Au in gold jewelry mainly takes density testing and X ray fluorescence spectrometer with energy dispersion (EDXRF). Density testing cannot detect gold jewelry alloy and demands that the jewelry shape is simple, while EDXRF is poor in penetration depth, which only can test on the sample surface and small area. This paper using the system programming controlled the vacuum system, the electronic balance, and EDXRF, and compared determination of Au by EDXRF( $w_{XAu}$ ) with the one by fire assay( $w_{Au}$ ) and the actual density ( $\rho$ ) by density testing with the theoretical density( $\rho_x$ ) calculated by the mathematical relationship between the crystallographic parameters and the content of gold and impurities for the samples. The results show while  $\rho_x - \rho / \rho_x$  is less than 0.4%, the equation of  $y$  ( $w_{XAu} - w_{Au}$ ) = - 0.4421 $x^2$  + 1.2534 - 0.0835 may correct for determination of Au by EDXREF, so create a set of testing device and provide an effective method for rapid determination of Au in gold jewelry, which can test simultaneously a mass of samples, and solve the disadvantages of density testing and EDXRF.

## Introduction

At present, determination of Au in gold jewelry mainly takes density testing, X ray fluorescence spectrometry (XRF), X ray fluorescence spectrometer with energy dispersion (EDXRF), electron probe spectroscopy (EMP-EDXRF), fire assay, induced-coupled plasma-atomic emission spectrometry (ICP-AES), and flame atomic absorption spectrometry (FAAS)[1]-[11], etc. These methods exist disadvantages. For example, density testing cannot detect gold jewelry alloy and demands that jewelry shape is simple; XRF, EDXRF, and EMP- EDXRF are poor in penetration depth, and can only test on sample surface and small area; fire assay, ICP-AES and FAAS are destructive test. Up to now, the literatures have not reported how combine effectively these methods so that form a comprehensive and rapid testing system. This paper using the system programming controlled the vacuum system, the electronic balance, and EDXRF, and compared the actual density ( $\rho$ ) with the theoretical density ( $\rho_x$ ) and determination of Au by EDXRF ( $w_{XAu}$ ) with the one by fire assay ( $w_{Au}$ ), so it creates a set of testing device, establishes a comprehensive method for rapid determination of Au in gold jewelry, solves the disadvantages of EDXRF, density testing and fire assay, and provides an effective rapid and synthesis way for determination of Au in gold jewelry alloys.

## Experiments

### Materials and Specimens

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

Table 1. The basic information of gold jewelry samples

No	Name	Quality (g)	No	Name	Quality (g)	No	Name	Quality (g)
1	Ring	5.274	5	Necklace	13.269	9	Necklace	8.895
2	Necklace	8.654	6	Bracelet	21.364	10	Necklace	8.649
3	Necklace	13.659	7	Bracelet	7.892	11	Necklace	12.679
4	Bracelet	10.064	8	Bracelet	9.897	12	Bracelet	10.679

## Instruments and apparatus

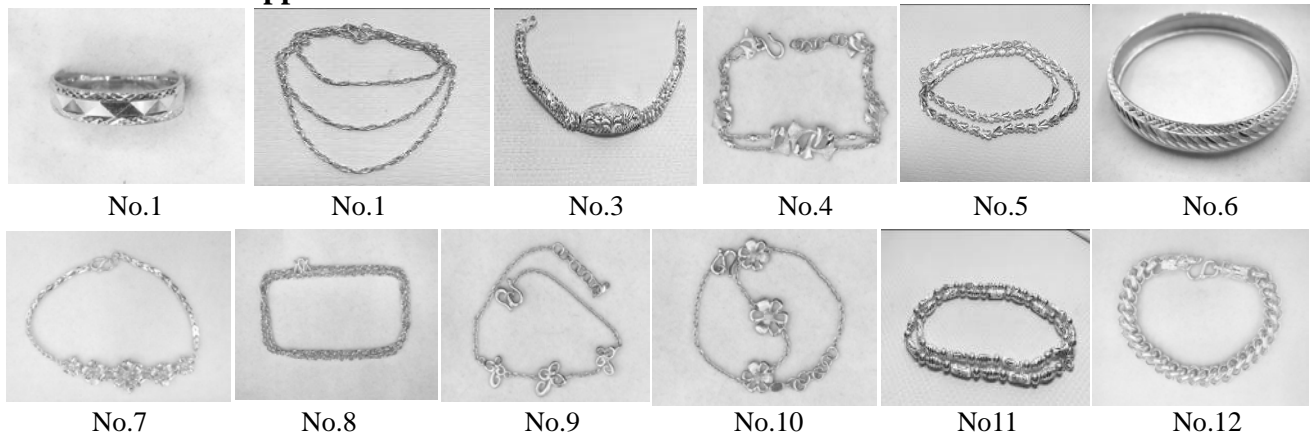


Fig.1. The photo of the gold jewelry samples

The EDXRF consisted of a Rh-anode side window low power X-ray tube (50W, 50kV, 2mA, 125  $\mu\text{m}$  Be window), a Si(Li) detector with 150eV FWHM at Mn  $K_{\alpha}$ , the range of analysis elements and determination of element content are from  $^{11}\text{Na}$  to  $^{92}\text{U}$  and from ppm to 100 %, respectively. Density testing system mainly consisted of the electronic balance with 0.1mg precision, the vacuum system by self-designed 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 $^{\circ}\text{C}$  and temperature difference less than 20  $^{\circ}\text{C}$ , 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

A mass of samples in air and in distilled water for extracting a certain vacuum degree (the sketch map of vacuum system by self-designed is shown in Fig. 2) can be weighted simultaneously by the set of device for synthesis and rapid determination of gold, so greatly improves the speed of density testing. This set of device using the system programming controlled the vacuum system, the electronic balance, and EDXRF, and compared determination of Au by EDXRF with the one by fire assay and the actual density ( $\rho$ ) by density testing with the theoretical density ( $\rho_x$ ) calculated for determination of gold and impurities by EDXRF in gold jewelry, and based on the fitting equations corrected for determination of Au by EDXRF. The principle of the set of device and the synthesis and rapid determination of Au in gold jewelry is shown in the Fig. 3.

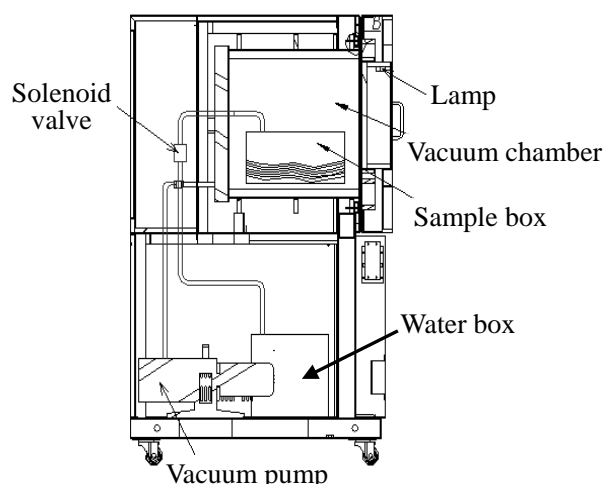


Fig.2. The vacuum system by self-designed

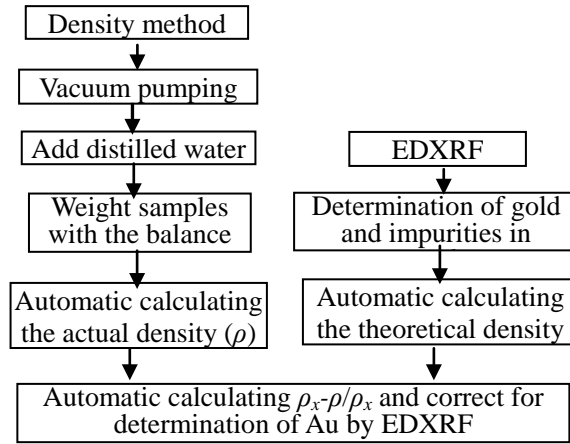


Fig.3. The principle of synthesis and rapid testing

## Results and Discussion

### Determination of actual density

According to the Archimedes's law, the sample density is determined by the following equation 1.

$$\rho = mp_1 / (m - m_1 + m_2) \quad (1)$$

There  $T$  is experiment temperature ( $^{\circ}\text{C}$ ),  $\rho$  is the actual density for the sample at  $T$   $^{\circ}\text{C}$  ( $\text{g}/\text{cm}^3$ ),  $m$  is sample weight in air ( $\text{g}$ ),  $m_1$  is the weight of specimen placed on the hanging wire in water ( $\text{g}$ ),  $m_2$  is the weight of hanging wire in water ( $\text{g}$ ),  $\rho_1$  is water density at  $T$   $^{\circ}\text{C}$  ( $\text{g}/\text{cm}^3$ ).

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

Table 2. The data on the samples by density testing

No	$m$	$T$	$\rho_1$	$m_1$	$m_2$	$\rho$	No	$m$	$T$	$\rho_1$	$m_1$	$m_2$	$\rho$
1	5.2740	15.7	0.9990	5.0430	0.0420	19.292	7	7.8921	16.2	0.9989	7.5209	0.0431	19.028
2	8.6541	16.0	0.9990	8.2457	0.0420	19.195	8	9.8970	17.0	0.9988	9.4220	0.0420	19.120
3	13.6590	15.8	0.9990	12.9914	0.0422	19.224	9	8.8951	14.6	0.9992	8.4653	0.0421	18.835
4	10.0642	16.2	0.9989	9.5831	0.0412	19.248	10	8.6490	15.1	0.9991	8.2336	0.0420	18.892
5	13.2691	15.3	0.9991	12.6165	0.0431	19.055	11	12.6790	15.3	0.9991	12.0499	0.0410	18.904
6	21.3640	15.8	0.9990	20.2902	0.0430	19.110	12	10.6790	15.3	0.9991	10.1574	0.0420	18.931

### Determination of theoretical density

Determination of gold and impurities by EDXRF in the samples are shown Table 3. There  $w_{\text{XAu}}$  is determination of Au by EDXRF.

Table 3. Determination of gold and impurities by EDXRF

No	$w_{\text{XAu}}$ (%)	$\text{Cu}$ (%)	$\text{Ag}$ (%)	$a_x \times 10^{-8} (\text{cm})$	No	$w_{\text{XAu}}$ (%)	$\text{Cu}$ (%)	$\text{Ag}$ (%)	$a_x \times 10^{-8} (\text{cm})$
1	99.90	0.00	0.10	4.076	7	99.00	0.50	0.50	4.069
2	99.72	0.00	0.28	4.076	8	99.20	0.40	0.40	4.070
3	99.60	0.00	0.40	4.076	9	98.00	1.00	1.00	4.062
4	99.81	0.00	0.19	4.076	10	98.10	1.00	0.90	4.062
5	99.10	0.50	0.40	4.069	11	97.96	1.04	1.00	4.061
6	98.95	0.50	0.55	4.069	12	98.20	1.00	0.80	4.062

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 the 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  $\rho_x$  can be obtained by the following equation 2.

$$\rho_x = \frac{M}{V} = \frac{m_p}{N_0 a_p^3 / 4} = \frac{4m_p}{N_0 a_p^3} \quad (2)$$

There  $M$  is gold atoms weight in gold unit cell,  $V$  is gold unit cell volume,  $N_0$  is the A Fugadero constant ( $6.022 \times 10^{23}/\text{mol}$ ),  $m_p$  is gold molar atomic weight (g/mol). The molar atomic weight of gold, silver and copper are 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 the lattice constant and quality. Based on Vegard low [12], the solid solution formed by components of same crystal structure is of a linear relationship as equation 3 between lattice parameters and components content. Because the lattice constant of gold unit cell ( $4.076 \times 10^{-8}$  cm) and the one of silver ( $4.086 \times 10^{-8}$  cm) is almost the same, regardless of silver atom displacement gold atom effected on the lattice constant, and only involved effect for cooper ( $3.615 \times 10^{-8}$  cm).

$$a_x = a_1 x_1 + a_2 x_2 \quad (3)$$

There  $\alpha_x$ ,  $\alpha_1$  and  $\alpha_2$  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 equation 3, and lattice constant  $a_x$  for the samples are shown in Table 3.

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

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

There  $m_p$  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 equation 4 into equation 1 and converted to equation 5. There  $\rho_x$  is the density of gold solid solution (gold jewelry alloy),  $N_0$  is the A Fugadero constant ( $6.022 \times 10^{23}/\text{mol}$ ),

$$\rho_x = \frac{m_p \cdot x_p + \sum_{i=1}^{n-1} m_i x_i}{\frac{1}{4} N_0 \cdot a_x^3} \quad (5)$$

$$m_p \cdot x_p + \sum_{i=1}^{n-1} m_i x_i = \frac{1}{4} N_0 \cdot a_x^3 \cdot \rho_x \quad (6)$$

$$x_p = \frac{\frac{1}{4} N_0 \cdot a_x^3 \cdot \rho_x - \sum_{i=1}^{n-1} m_i x_i}{m_p} \quad (7)$$

Impurity i atom percent can be obtained by the following equation 8. There  $w_i$  is impurity i weight percent,  $w_p$  is gold weight percent.

$$x_i = \frac{\frac{w_i}{m_i}}{\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p}} \quad (8)$$

Intrduced equation 8 into equation 7 and converted to equation 9.

$$x_p = \frac{\frac{1}{4} N_0 \cdot a_x^3 \cdot \rho_x - \sum_{i=1}^{n-1} \frac{w_i}{\sum_{i=1}^{n-1} \frac{w_i}{m_i} + \frac{w_p}{m_p}}}{m_p} \quad (9)$$

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

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

Intrduced equation 6 into equation 10 and converted to equation 11.

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

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

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

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

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

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

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

$$\rho_x = \frac{4m_p}{(w_p + m_p \sum_{i=1}^{n-1} \frac{w_i}{m_i}) N_o a_x^3} \quad (14)$$

Introduced determination of Ag and Cu by EDRXF (shown in table 3) and corrected  $a_x$  (shown in table 3) into Eq. 14, and theoretical density  $\rho_x$  for the samples are shown in Table 4.

Table 4. The theoretical density obtained by equation 14 (g/cm<sup>3</sup>)

	No1	No2	No3	No4	No5	No6	No7	No8	No9	No10	No11	No12
$\rho_x$	19.304	19.275	19.256	19.289	19.155	19.131	19.139	19.180	18.965	18.980	18.963	19.000

### Determination of gold by fire assay

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

$$W_{Au} = \frac{m_2 + \Delta m}{m_1} \times 100 \quad (15)$$

There  $w_{Au}$  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). There  $m_3$  is the quality of standard gold specimen (mg),  $m_4$  is the standard gold specimen quality of separated impurities (mg), E is purity of standard gold specimen (%). Determination of Au by fire assay are shown in Table 5.

Table 5. Determination of Au in the samples by cupellation method(%)

	No1	No2	No3	No4	No5	No6	No7	No8	No9	No10	No11	No12
$w_{Au}(\%)$	99.89	99.37	99.50	99.64	98.60	98.90	98.47	99.00	97.47	97.71	97.71	97.90

## Discussion

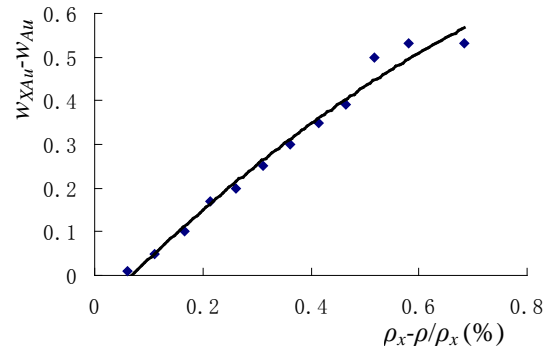


Fig.4. The curve between  $\rho_x - \rho / \rho_x$  and  $w_{XAu} - w_{Au}$

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 content of gold is higher tested by EDXRF than by cupellation method, it is reason that EDXRF does not detect the part with solder, and as the extension of  $\rho_x - \rho / \rho_x (x)$ ,  $w_{XAu} - w_{Au} (y)$  increases (that is, the less  $\rho_x - \rho / \rho_x$ , the more reliable the result by EDXRF). The fitting equation and the curve between  $\rho_x - \rho / \rho_x (x)$  and  $w_{XAu} - w_{Au} (y)$  are shown in equation 16 and Fig.4, respectively. Known from Fig.4, as  $\rho_x - \rho / \rho_x (x)$  is less than 0.4 %, the curve is almost consistent with the testing data, so based on equation 16, it may correct for determination of Au by EDXRF. While  $\rho_x - \rho / \rho_x (x)$  is more than 0.4 %, the testing data and the curve is of large difference, which maybe caused by more impurities.

$$y = -0.4421x^2 + 1.2534x - 0.0835 \quad (98.00 \% \leq Au < 99.99 \%) \quad (16)$$

Table 6. The data by EDXRF and density testing and fire assay and Eq. 15

No	Basic information		EDXRF		Density testing		Cupellation	$w_{XAu} - w_{Au}$
	Name	$m$ (g)	$w_{XAu}$ (%)	$\rho_x$ (g/cm <sup>3</sup> )	$\rho$ (g/cm <sup>3</sup> )	$\rho_x - \rho / \rho_x$ (%)	$w_{Au}$ (%)	(%)
1	Ring	5.2740	99.90	19.304	19.294	0.062	99.89	0.01
2	Necklace	8.654	99.72	19.275	19.195	0.420	99.37	0.35
3	Necklace	13.659	99.60	19.256	19.224	0.166	99.50	0.10
4	Bracelet	10.064	99.81	19.289	19.248	0.213	99.64	0.17
5	Necklace	13.269	99.10	19.155	19.055	0.517	98.60	0.50
6	Bracelet	21.364	98.95	19.131	19.110	0.110	98.90	0.05
7	Bracelet	7.892	99.00	19.139	19.028	0.580	98.47	0.53
8	Bracelet	9.897	99.20	19.180	19.120	0.261	99.00	0.20
9	Necklace	8.895	98.00	18.965	18.835	0.685	97.47	0.53
10	Necklace	8.649	98.10	18.980	18.892	0.464	97.71	0.39
11	Necklace	12.679	97.96	18.963	18.904	0.311	97.71	0.25
12	Bracelet	10.679	98.20	19.000	18.931	0.363	97.90	0.30

## Conclusion

The method for rapid and synthesis determination of Au solves the disadvantages which EDXRF only detects on gold jewelry surface and small area, and density testing cannot detect gold jewelry alloys and demands that jewelry shape is simple, which can test simultaneously a mass of samples, and provides an effective rapid and synthesis way for determination of Au in gold jewelry alloys.

Using the system programming controlled the vacuum system, the electronic balance, and EDXRF, and compared the actual density ( $\rho$ ) by density testing with the theoretical density ( $\rho_x$ ) calculated for determination of Au and impurities by EDXRF and corrected  $a_x$  in gold jewelries. If  $\rho_x - \rho / \rho_x$  is less than 0.4%, based as the equation of  $y = -0.4421x^2 + 1.2534x - 0.0835$  ( $98.00 \% \leq Au < 99.99 \%$ ) may correct for determination of Au by EDXRF, so the rapid and synthesis way for determination of Au in gold jewelry alloys is effective and reliability.

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