

Promotion of the Cupellation Method for Accurate Determination of Gold Alloy's Karat Containing Platinum-Group Metals

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ABSTRACT: *The main standard method for gold karat determination is the cupellation method. However, this method is not sufficiently accurate to determine gold karat in the presence of insoluble Platinum-Group Metals (PGMs), such as Ir, Ru, and Rh. In this study, for the first time, a complementary method which can be used in coupled with the reference cupellation method is presented for highly accurate determination of gold karat containing PGMs. According to this method, gold metal was separated from the PGMs by dissolving parted cornets in aqua regia and then, its selective precipitation using an aqueous solution of SO₂ gas as a reducing agent. The gold amount in alloys containing PGMs was determined using the suggested strategy with an excellent recovery, high accuracy (average relative error=0.12%) and precision (SD=0.6 for n=3). The optimized volume of aqueous SO₂ solution was 35 mL that provides a gold recovery as high as 99.7% with enough big grain size and high purity (999.0‰). The proposed strategy was successfully used to determine the gold amount in secondary gold jewelry containing Ir, Rh, and Ru (a gold recovery of 99.9% with a relative error of 0.07 was obtained). The obtained karat was comparable with the other methods. Accordingly, the proposed method will be a promising simple and available assay for gold alloys containing PGMs, which could be used routinely in most cupellation labs all over the world.*

KEYWORDS: *Cupellation method; Platinum-group metals; Gold karat; Gold alloys.*

INTRODUCTION

In manufacturing gold jewelry, it is common to add some alloying metals (such as Cu, Zn, and Ag) to pure gold to increase the mechanical and durability of jewelry, change colors and reach to the official gold karat of each country. Therefore, the determination of karat of gold alloys, which represents the weight of gold

content with respect to the total weight of the alloy, is a central function in manufacturing and distributing jewelry as well as brokering and refining related gold karat scraps and wastes [1]. Cupellation method (fire assay), which is defined in international standard ISO11426 [2], is commonly used as an accepted reference

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method for the determination of gold karat. It is a cost-effective, highly precise and accurate, and available method for gold alloys containing Ag, Cu, and Zn. Some modifications in this method are performed for white gold alloys consisting of Ni and/or Pd. However, this method is not sufficiently accurate to determine gold karat in the presence of insoluble Platinum-Group Metals (PGMs) such as rhodium (Rh), ruthenium (Ru) and iridium (Ir). Because they aren't separated from gold during cupellation, and hence remain in the final gold pieces [3]. Therefore, the gold karat is incorrectly determined higher than its actual amount, which confuses operators of cupellation labs and makes systematic errors in the test results.

The addition of the PGMs (Ir, Ru, and Rh) to gold alloys is rarely done in the manufacture of gold jewellery since they cause hardening of the gold alloys and damaging of goldsmith's tools [4, 5]. Nevertheless, there are amounts of these metals in most of gold jewellery. They are entered into gold alloys in different ways. For example, Rh is usually used for plating of white gold jewellery and Ir and Ru are added as grain refiner to the molten gold alloys [6]. Moreover, some of the gold manufacturers add illegally some amounts of these elements instead of pure gold to the gold articles in order to obtain more profits. Approximately, each ounce of pure gold costs about 2 times higher than one ounce of the PGMs. Therefore, economically and legally, it is important to recognize the presence of these PGMs in the gold alloys and then remove and determine them. In some laboratories, modern sensitive methods such as X-Ray Fluorescence (XRF) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are used for the gold assay alone or along with the cupellation method [7, 8]. However, they are expensive and/or rarely available for most commercial gold assay laboratories. Therefore, the improvement and correction of the cupellation method, so that could correctly determine the karat of gold pieces containing the PGMs, can be helpful.

In this study, a simple and available strategy was exhibited for the separation of the PGMs (Ir, Ru, and Rh) from the gold matrix of cornets for highly accurate determination of gold karat. After the usual cupellation and parting processes, aqua regia solution was added to the gold cornets containing the PGMs to dissolve its gold content. After removing the undissolved PGMs in aqua

regia, various reducing agents were considered for the selective precipitation of gold. Among them, an aqueous solution of SO₂ gas was selected as the best one. Then, the effect of the consumed volume of SO₂ solution on the gold recovery and the size of gold particles was investigated. Using this strategy, the karat of the gold alloys containing the PGMs was determined with high accuracy and precision. Finally, the performance of the proposed method was compared with the other methods.

EXPERIMENTAL SECTION

Materials and apparatus

Ru, Rh and Ir powder with a high purity (99.9%) was purchased from Sigma-Aldrich. The other used chemicals were of analytical grade and obtained from Merck. The surface morphology and chemical composition of the samples were investigated using a Scanning Electron Microscope (SEM, Coxem-CX100), energy-dispersive X-ray spectroscopy (EDS) and X-Ray Fluorescence (XRF, OLYMPUS SDD).

Sampling and cupellation process

In this study, it was used a gold ingot with 999.9‰ karat, three gold alloys containing Rh or Ru or Ir, and a secondary (Au-Ir -Ru-Rh) jewellery with definite chemical compositions. These articles were made by induction melting of metals powder in a crucible under argon. Then, it was poured into a steel mould until cooled. Afterwards, 235.0 mg of each type of sample according to the International Standard ISO11426, was weighed by means of precision balance sensitive to the hundredth of mg. Then, sampling is carried out according to the procedure reported in the International Standard ISO11596 [9].

The cupellation process was performed according to the ISO11426 Standard. Briefly, at the first stage (the so-called cupellation stage) pure Ag equivalent to 2.5 times of the mass of fine gold (0.44062 g for gold alloys with 750.0‰ karat and 0.58744 g for the gold ingot with 999.9‰ karat) was added to the samples. Then, they were wrapped in pure lead foil into a tight ball. Then, it was cupelled in a cupellation furnace at 1150°C for 25 minutes under oxidizing conditions until a precious metal bead was obtained. At such a high temperature, except PGMs and noble metals (such as Au, Ag and Pd) all base metals (such as Cu and Zn) are oxidized.

Therefore, they are absorbed by the cupel surface, whereas noble metals remain in the form of metal beads. Afterwards, the obtained beads were flattened and rolled. In the next stage (the so-called cornet stage), extracting (parting) of Ag in 20 mL of 33% nitric acid solution was done. Finally, the obtained gold cornets were transferred into crucibles, annealed (500-850 °C for 5 min) and cooled.

PGMs separation and gold refining

At the first, the parted cornets were dissolved in concentrate HCl and HNO₃ mixture with a volume ratio of 3:1 (the so-called aqua regia). Each 0.5 g cornet was dissolved in 4.0 mL aqua regia. Unlike gold, the PGMs were not dissolved in aqua regia. They remained as solid pieces on the bottom of the container. Then, the PGMs solids were separated from the gold solution through filtering. In the next step, aqua regia was evaporated by heating. This step is necessary because it is well-known that reducing agents are effective only in the absence of dissolved nitrogen oxides [10].

The residue was dissolved in 100 mL aqueous solution containing of 0.4 M HCl, and then gold was participated using SO₂ gas or aqueous SO₂ solution. To prepare an aqueous SO₂ solution, concentrated H₂SO₄ has added dropwise into sodium metabisulfite (Na₂S₂O₅) solution, and simultaneously, the released SO₂ gas was transmitted into a closed container containing distilled water via a tube. After water was adequately saturated with SO₂ gas (i.e. when pH reached to about 1), a proper volume of aqueous SO₂ solution (optimized volume=35 mL) was added to the gold solution in aqua regia until gold was selectively precipitated. Finally, the gold sediment was filtered off, washed and dried. If it was needed, the resultant powder was melted to a solid button or ingot.

To participate gold using oxalic acid as the reducing agent, after removing all nitrogen oxides from the gold solution, it was diluted to 100 mL with distilled water. Afterwards, 2 mL concentrated HCl, 5 drops of concentrated H₂SO₄ and 3 mL oxalic acid solution (10% w/v) were added and placed on a steam bath overnight. Then, it was filtered using a filter paper and then washed, transferred to a porcelain crucible and ignited to the metal. Then, the crucible was cooled and weighed.

To participate gold using hydroquinone, 1 mL of concentrated HCl per 100 mL of the residue was added and

then heated to boiling. 3 mL of 1 % aqueous hydroquinone solution (freshly prepared) was added dropwise into the solution stirring continuously. After boiling for 15 min, it was placed on a steam bath for 30 min to coagulate the gold precipitate. Then, it was cooled and filtered immediately. The filter paper was transferred to a porcelain crucible and ignited in a furnace, cooled and weighed.

RESULTS AND DISCUSSION

Chemical and morphological studies of Au-PGMs beads and cornets

Drawing the distribution plot of PGMs in the bead is a rational approach to minimize the chance of error in detection of Ir, Ru, and Rh in karat gold. Therefore, to find how the PGMs are distributed throughout the beads, PGMs amount along the cutted vertical section from top part of the beads surface to bottom was followed using XRF analysis, and then the average amount was plotted versus distance from the top of the bead. Fig. 1 shows that the negligible amounts of PGMs are present at the bottom of the bead. The distribution plot of Ir is very different from that for Ru and Rh. As it is clearly seen, very low amounts of Ir are found on the surface, but there is its significant amount in the inner parts of the bead, which increases slowly with increasing distance from the top of the bead up to 75% distance. However, Ru is present at its maximum amount on the bead surface and decreases with increasing distance from the top of the bead. It can be observed that Rh is absent at the bottom of the bead. The non-uniform distribution of the PGMs along the vertical section of the beads can be due to their low solid solubility in Au and Ag. Since the density of Ru and Rh (12.4 and 12.1 g/cm³) is lower than the average density of other metals of the bead alloy (~14.9 g/cm³), they accumulate more on the surface or center of the bead. Despite Ru and Rh, Ir has a higher density (22.5 g/cm³) than the average density of the bead alloy. Therefore, it exhibits a different distribution plot and its amount is negligible on the surface of the bead. The distribution plots of PGMs in Fig. 1 is helpful to identify areas that are rich in PGMs, where the further studies were performed.

The SEM image taken from the inner parts of the cutted vertical section of the bead containing Ir in Fig. 2a shows that there are some small discrete micro segregations as platelets. The obtained EDS analysis reveals that they are

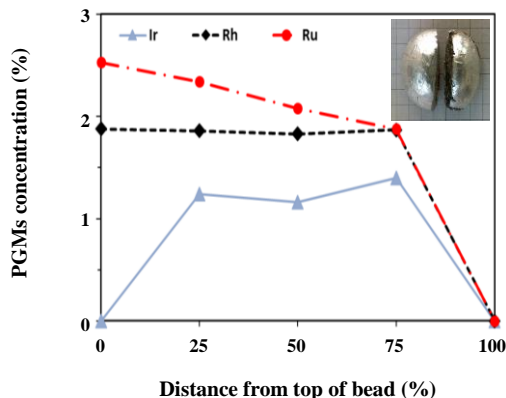


Fig. 1: PGMs concentration along the cutted vertical section of the Au-Ir, Au-Rh and Au-Ru beads; (The inset: Photograph image of the Au-Ir bead).

mainly composed of Ir. A possible explanation for this behavior is that Ir has a high melting point (2446 °C) in comparison with Au (961.7 °C) and Ag (1064 °C) and exhibits low solid solubility in Au. Therefore, it cannot be interacted and/or entered into Au matrix and hence forms discrete phases [11-13]. After parting, as shown in Fig. 2b, the morphology of Au matrix changes completely so that it appears as sponge-like (granular) nanostructures with a uniform granule size. In some places, some surrounded angular plates are also seen, which corresponding EDS analysis indicates that they are composed of Ir. Moreover, it is seen no Ag peak in EDS spectra, which shows that Ag is removed completely from the alloy. Generally, nitric acid does not dissolve Au and Ir but dissolves Ag. Therefore, with the removal of Ag from the homogeneous Au-Ag alloy, the cavities appear. On the other hand, the absence of holes or pores on the angular plates confirms that Ir doesn't form an alloy with Ag in the condition of the cupellation process. A nearly similar morphology is seen for the annealed parted cornet (Fig. 2c). Off course, the sponge-like structure becomes more open. In other words, the size of the pores increases. The corresponding EDS analysis shows that the surrounded plates are from Ir, which has remained in the same places, but their surface seems to be rougher and their shape becomes irregular. All of these results indicate that Ir does not remove from the gold alloy during all the stages of the cupellation and parting processes.

It was also obtained SEM images and corresponding EDS analysis for the gold sample containing Rh after

the formation of the bead and annealed cornet. As shown in Fig. 3, discrete micro segregations of Rh are distributed in the compact matrix of gold. This is confirmed by the related EDS spectra which exhibits both of the Rh and Au peaks. Fig 4a illustrates the SEM image of annealed Au-Rh cornet. The EDS spectra were obtained from two marked parts in Fig. 4a. Fig. 4b and c show that part 1 (the micro segregations) and part 2 (sponge-like structures) are composed of mainly from Rh and Au, respectively. Similar to Ir, the Rh micro segregations become rough and the sponge-like structure of Au matrix appears after parting and annealing processes. The similar morphological structures were seen for Au-Ru bead and cornet (not shown). These observations show that although the surface morphology of the beads and cornets obtained from Au-Ir, Au-Rh, and Au-Ru is a bit different, they exhibit similar behavior during cupellation and parting processes. All of them remain in the finally obtained cornet and thereby cause the gold karat is calculated incorrectly higher than its actual amount.

The surface morphology of a secondary gold jewellery containing a large amount of Rh and low amount of Ru and Ir after parting and annealing processes was also investigated using SEM. As shown in Fig. 5a, many plates with different shapes and sizes are surrounded by gold sponge-like structures. The EDS analysis in Fig 5b and c indicate that these plates are mainly composed of Rh. Although Ir and Ru peaks are not observed in EDS spectra in Fig 5b, Ir and Ru are recognized from EDS in Fig 5c. This indicates that the simultaneous presence of Rh, Ir, and Ru causes no significant change in the surface morphology of the annealed cornets.

The refining of gold cornets containing PGMs

As shown in the previous section, the PGMs remain in the gold articles after the cupellation and parting processes. Therefore, the PGMs should be removed from Au matrix by employing a suitable refining procedure. There are various techniques which are usually used for recovering gold, such as Fizzer cell, Wohlwill electrolytic, Pyrometallurgical and aqua regia process [14, 15]. Among them, the aqua regia process was selected as a simple and available method for the PGMs separation from gold, since dislike gold and base metals such as Ag, Cu, and Ni, the PGMs are not dissolved in aqua regia. Moreover, this process, which is the most widely used

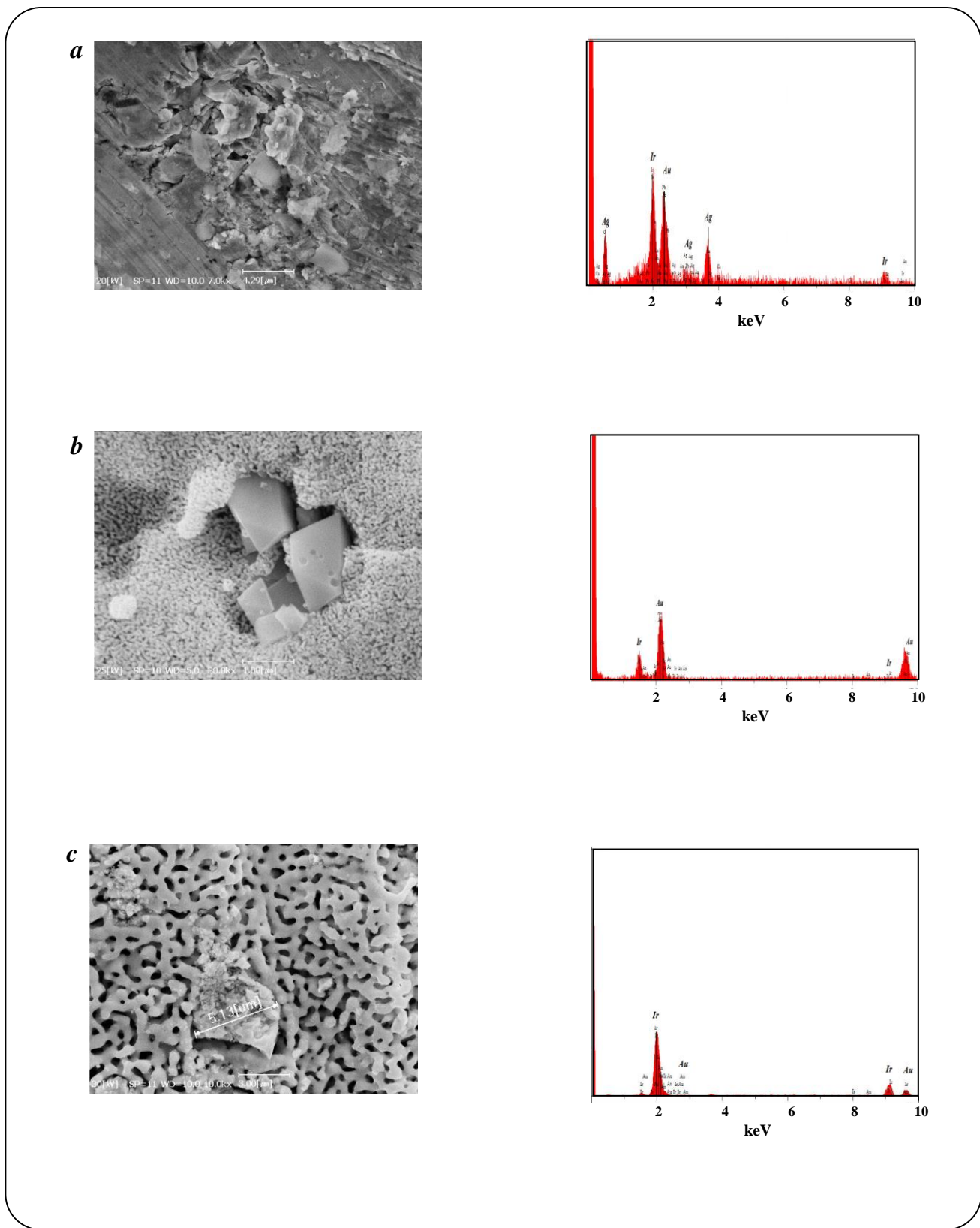


Fig. 2: SEM images and EDS analysis of Au-Ir after the formation of the bead (a), parted cornet before (b) and after (c) annealing

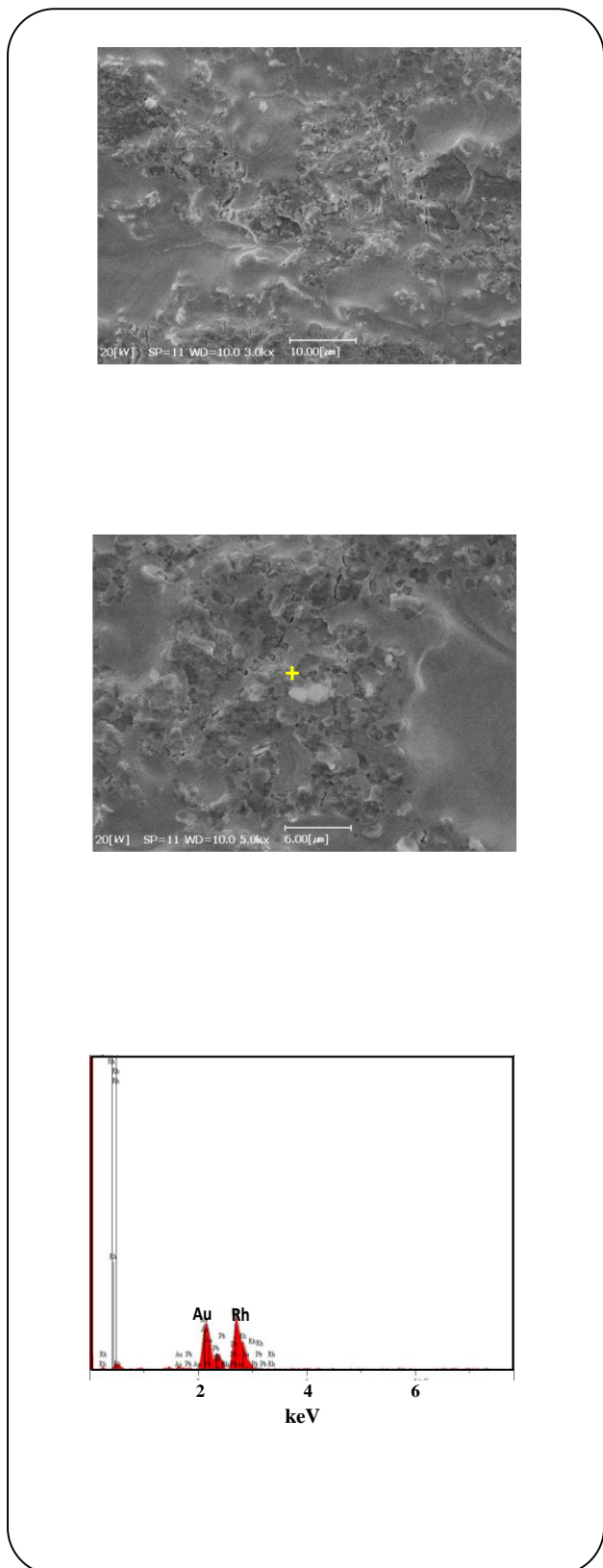


Fig. 3: SEM images and related EDS analysis of Au-Rh after the formation of the bead.

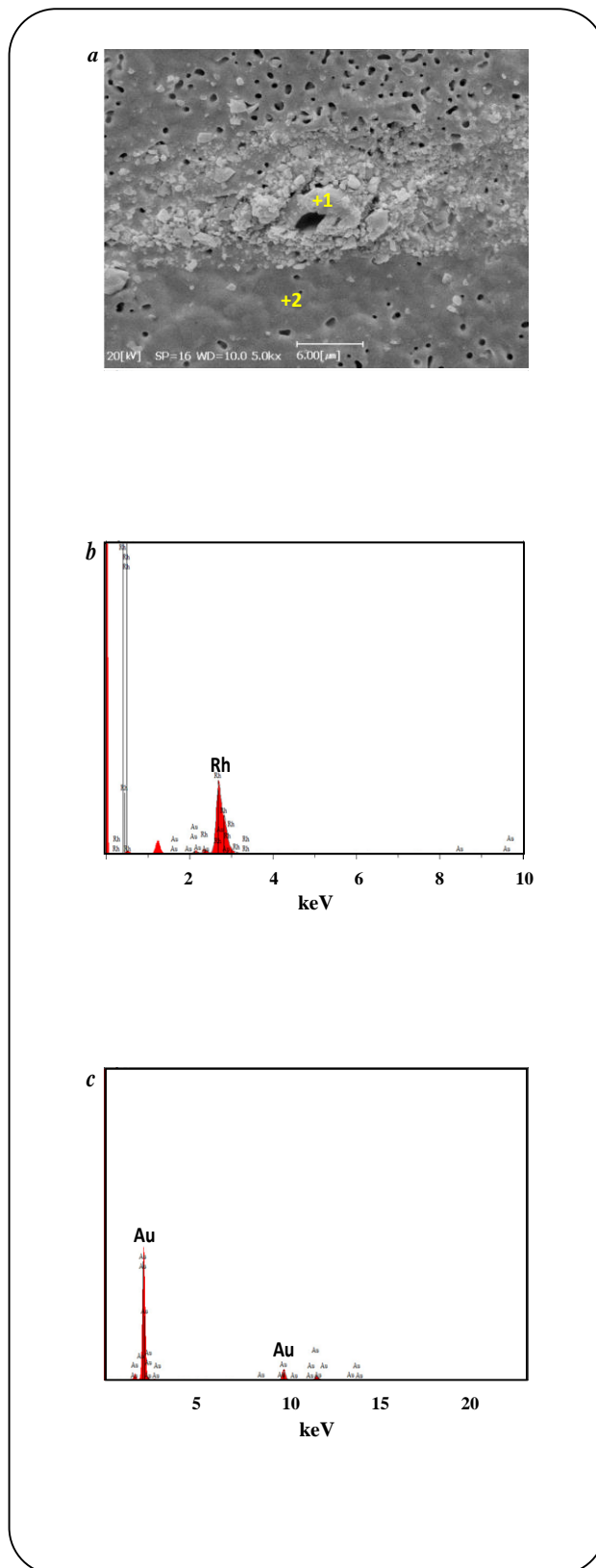


Fig. 4: SEM image (a), and EDS spectra of part 1 (b), and part 2 (c) of Au-Rh sample after parting and annealing.

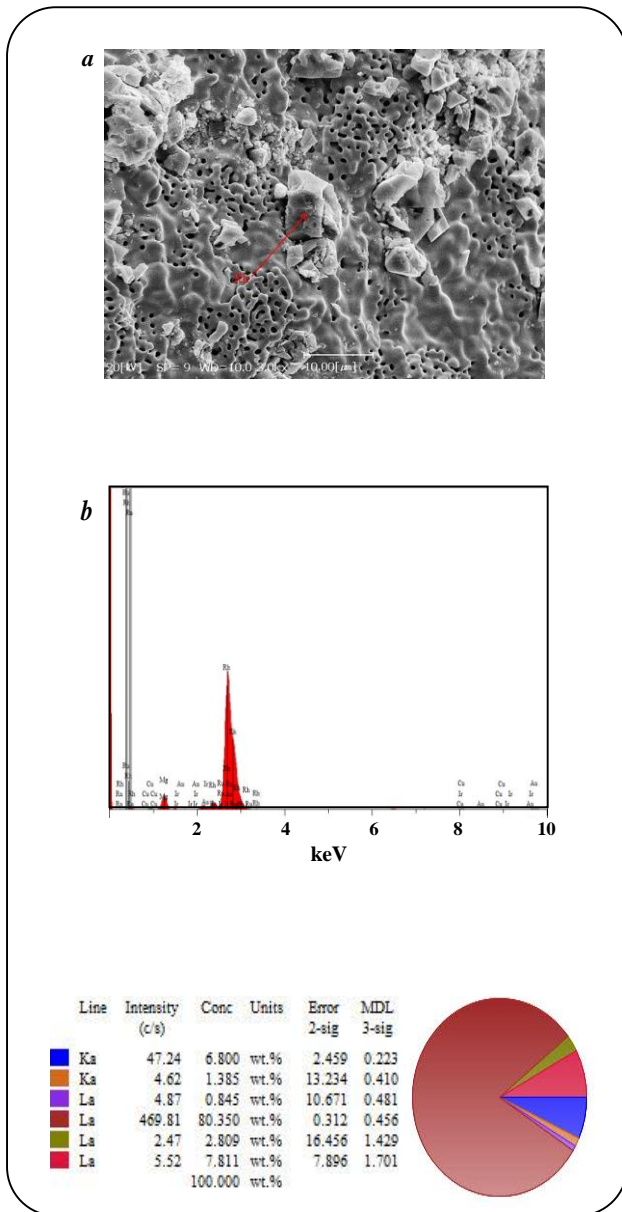


Fig. 5: SEM image (a), and EDS results (b, c) of a secondary gold jewelry containing Ir, Ru and Rh after parting and annealing.

at the small-medium scale by jewellers and refineries alike, can produce gold of up to 99.99% purity [15] and be used in laboratories for the recovery of low amounts of gold (in the scale of mg). Moreover, it can complete and be compatible with the international standard cupellation method. A disadvantageous of this process is that it can be used only when initial silver content is less than 10%, because AgCl is co-precipitated with Au, and thereby reduces the purity of gold [16]. This problem

doesn't matter in our suggested procedure, since all Ag contents are removed from Au matrix in the parting stage. Accordingly, this method is suitable to couple with cupellation method for the PGMs separation from the gold cornets. Inexpensive cost, time saving, and reduced health, safety, and environmental problems were other important parameters that were considered when choosing the method.

After the gold cornet dissolution and separation of the PGMs, gold metal must selectively participate from the spilled solution by a reducing agent. Selecting a proper reducing agent is very important since it has significant effects on purity, physical form and the reduction rate of gold. Hydrazine, formaldehyde, oxalic acid, hydroquinone, sodium bisulphite and sulphur dioxide (SO₂) gas are reducing agents which are usually used for gold refining [10]. In Table 1, the advantageous and disadvantageous of some of them have been summarized. Among them, it was decided to use SO₂ gas, because the precipitation need not involve the presence of a salt. Moreover, it is an economic way that is suitable for quantities of gold of 100 mg [10]. Also, the presence of Pt and Pd, which can contaminate the participated gold, does not create any problem for our work, because these metals (if any) are leached in the parting stage. To further investigate, the gold recovery of the method performed using SO₂ gas was compared with that using oxalic acid and hydroquinone. Accordingly, a spilled gold solution was divided into three equal parts, and then the gold of each part was participated separately using the reducing agent. The obtained gold metal was determined and finally, gold recovery percent was estimated according to the equation (obtained Au amount/added Au amount)×100. This experiment was repeated for another spilled gold solution. The obtained results in Table 2 show that the use of SO₂ gas exhibits the highest recovery in comparison with oxalic acid and hydroquinone. This confirms that SO₂ gas is a proper reducing agent that can be used for gold participation in this work.

A major problem during SO₂ gas blowing was the accumulation of gold particles into the gas blower tube, which resulted in the loss of a huge amount of gold, and hence an error in the estimation of gold karat. To overcome this problem, it was used water saturated with SO₂ gas instead of direct blowing of SO₂ gas. For this purpose, concentrated H₂SO₄ is added dropwise into sodium metabisulfite (Na₂S₂O₅) solution, and

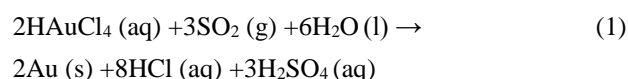
Table 1: Advantageous and disadvantageous of various reducing agents [15].

Reducing agent	Advantageous	Disadvantageous	E ⁰ (V)
Tetraethyl ammonium chloride	Less time to determine gold in the presence of PGMs/ Suitable after initial precipitation with SO ₂	Inappropriate for quantitative tests	-
Hydroquinone	Suitable for determination of 1-50 mg gold/ Selective precipitation of gold from an acidic solution containing Ni, Cu, Zn, Pt, and Pd	Not suitable for determination of gold more than 50 mg	+0.70
SO ₂ (g)	Not involve the presence of a salt / Less interference of Pd with respect to hydroquinone	Pd and Pt contaminate the participated gold	+0.17
Oxalic acid	Suitable for precipitation of gold higher than 10 mg in the presence of the other noble metals, especially Pt/ No problem in the presence of its excess amounts	Formation of very fine gold precipitations	-0.49

Table 2: Recovery comparison of various reducing agents.

Reducing agent	Added Au amount (gr)	Recovered Au amount (gr)	Recovery (%)
Hydroquinone	0.4533	0.4501	99.29
	0.3722	0.3698	99.35
SO ₂ (g)	0.4530	0.4528	99.95
	0.3720	0.3719	99.97
Oxalic acid	0.45310	0.4406	97.24
	0.3725	0.3610	96.91

simultaneously, the released SO₂ gas is transmitted into a closed container containing distilled water via a tube. After water is adequately saturated with SO₂ gas (i.e. when pH reaches to about 1), it is added to the gold solution in aqua regia. Gold ions are participated *via* aqueous SO₂ solution according to the following equation:



The effect of aqueous SO₂ solution volume

To achieve the highest gold recovery, accuracy, and precision, the aqueous SO₂ solution volume added to the aqua regia solution was optimized. As it can be seen in Table 3, at very low volumes (5.0 and 10.0 mL) no gold is recovered. As the volume increases, the gold recovery is also enhanced, so that at volumes higher than 30 mL, the recovery is obtained more than 99%. In addition to gold recovery, the grain size of the obtained gold powder was another factor that must be considered. Fig. 6 shows the grain size of the gold powder recovered at different volumes of aqueous SO₂ solution. The difference between the size of the small and big particles is well observable in

this figure. At 15 and 20 mL, very fine gold grains are formed. By increasing the volume, they become bigger until at 45 and 50 mL the granule gold with the size of 45 μm is obtained. It should be noted that the accumulation of gold powder with bigger grain size is easier. Nevertheless, 35 mL was selected as the optimized volume, since it exhibits the highest recovery and enough big gold grain size. Moreover, the precision of the proposed method was investigated by the determination of the standard deviation. The obtained values show that the proposed method exhibits an acceptable precision. The lowest value for SD (0.6) is obtained at 35 mL, indicating the best precision.

The efficiency of the suggested method was investigated by the determination of Au, Ir, Ru and Rh amount in the laboratory-made gold articles (Table 4). The comparison of the obtained values with the added amounts shows that the proposed procedure exhibits an acceptable recovery for gold and the PGMs. An excellent recovery percent was obtained (between 99.9 and 100.1 for Au). Also, the average relative error was 0.12% for Au, indicating the high accuracy of the method. Moreover, gold is determined in a secondary gold

Table 3: The effect of added aqueous SO₂ solution on the gold recovery and grain size.

Added aqueous SO ₂ solution volume	pH	Added gold amount (g)	Recovered gold amount (g)	Gold recovery (%)	Average gold recovery (%) \pm ts/ \sqrt{n} (t=4.3, n=3)	Gold grain size	Standard deviation (n=3)
5.0	0.67	0.5404	-	-	-	-	-
10.0	0.77	0.5405	-	-	-	-	-
15.0	0.86	0.5304	0.0783	14.8	14.8	Very fine	-
20.0	0.93	0.5407	0.0831	15.4	15.4	Very fine	-
25.0	1.03	0.5404	0.5271	97.5	98.9 \pm 4.0	Fine	1.6
		0.6041	0.6081	100.7			
		0.0870	0.0858	98.6			
30.0	1.23	0.5267	0.5257	99.8	99.1 \pm 3.6	Big	1.4
		0.6246	0.6081	97.4			
		0.1116	0.1116	100.0			
35.0	1.38	0.5264	0.5213	99.0	99.7 \pm 1.4	Big	0.6
		0.6083	0.6084	100.0			
		0.2795	0.2795	100.0			
40.0	1.53	0.5371	0.5374	100.0	99.4 \pm 1.8	Big	0.7
		0.6040	0.6008	99.5			
		0.0070	0.0069	98.6			
45.0	1.62	0.5297	0.5274	99.6	99.4 \pm 1.6	Granule (45 μ m)	0.6
		0.6045	0.6037	99.9			
		0.0079	0.0078	98.7			
50.0	1.62	0.5329	0.5341	100.2	98.6 \pm 5.9	Granule (45 μ m)	2.4
		0.6017	0.6005	99.8			
		0.0068	0.0065	95.9			

**Fig. 6: The grain size of the gold recovered at different aqueous SO₂ solution volumes.**

Table 4: The performance study of the proposed method.

Sample	Element	Added amount (gr)	Recovered amount (gr)	Recovery (%)	Relative error (%)
Lab-made Au ingot	Au	0.5119	0.5110	99.8±0.13	0.17
Lab-made Au-Rh article	Au	0.5157	0.5162	100.1±0.17	0.09
	Rh	0.0415	0.0416	100.2±0.21	
Lab-made Au-Ir article	Au	0.5110	0.5117	100.1±0.15	0.13
	Ir	0.0400	0.0393	98.3±0.19	
Lab-made Au-Ru article	Au	0.5120	0.5127	100.1±0.22	0.13
	Ru	0.0428	0.0426	99.5±0.25	
Secondary(Au-Ir-Ru-Rh) jewellery	Au	0.5254	0.5250	99.9±0.18	0.07
	Ir+Rh+Ru	0.04257	0.04202	98.7±0.20	

jewellery containing Ir, Rh, and Ru using the suggested method, which was 0.5250 g, which is very close to the added gold amount (0.5254 g). A recovery of 99.9% and a relative error of 0.07 were obtained. This indicates that using the proposed method the PGMs can be separated from gold jewellery and ingots with a high accuracy, and hence the weight of the obtained pieces can be considered nearly equal to the weight of pure gold.

As mentioned in the international standard ISO11426 [2], the following equation can be used for the calculation of gold content in a gold sample.

$$W_{Au} = \frac{m_1}{m_2} \times F \times 10^3 \quad (2)$$

Where m_2 is the mass of the gold sample, m_1 the mass of the sample cornet and F the mean value of the proof assay sample factors. However, according to the results of section 3.1, m_1 cannot reflect the real mass of gold in gold alloys containing the PGMs. As a consequent, ISO11426 must be corrected for gold alloys containing the PGMs in such a way that m_1 must be obtained after further purification of the cornets using our proposed method.

The performance comparison of the suggested method with other methods

The performance of the suggested method with

the other methods was compared by determining the karat of gold samples containing different PGMs. As it is evident in Table 5, the suggested method exhibits a response with a high accuracy and precision and is comparable with the other methods. This indicates that this method has a great potential to determine the karat value in the gold jewellery containing the PGMs.

CONCLUSIONS

This work exhibits a simple and available strategy for the separation of PGMs like Ir, Ru, and Rh from gold matrix of cornets. The PGMs can be separated from the gold matrix by dissolving the parted cornets in aqua regia and then selective precipitation of gold using aqueous SO_2 solution. A gold recovery more than 99% with enough big grain size and high purity (999.0‰) are obtained using this strategy. Moreover, the karat gold obtained using this method is comparable with that of the other methods. Accordingly, this strategy can be used in coupled with the cupellation method for highly accurate and precise determination of karat of gold alloys containing Ir, Ru and Rh.

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Table 5: The performance comparison of the proposed method with the other methods.

Sample	Element	Added gold amount (gr)	Actual karat	Karat by XRF	Karat by cupellation method \pm ts/ \sqrt{n} (t=4.3, n=3)	Karat by the proposed method \pm ts/ \sqrt{n} (t=4.3, n=3)
Lab-made Au	Au	0.5130	998.0	999.90 \pm 0.03	999.33 \pm 1.03	998.1 \pm 0.25
Lab-made Au-Rh	Au	1.0017	926.9	930.50 \pm 0.01	998.90 \pm 0.25	927.00 \pm 2.48
	Rh	0.0789	73.01	69.50 \pm 0.05	-	-
Lab-made Au-Ir	Au	0.4683	943.00	946.00 \pm 0.02	997.99 \pm 1.51	942.00 \pm 2.50
	Ir	0.0284	57.10	54.00 \pm 0.01	-	-
Lab-made Au-Ru	Au	0.3696	972.00	977.7 \pm 0.04	995.90 \pm 0.25	969.90 \pm 1.96
	Ru	0.0107	28.10	22.3 \pm 0.05	-	-
Secondary jewellery Au-Ir-Cu-Ag	Au	1.1559	763.16	764.00 \pm 0.02	783.90 \pm 0.37	762.06 \pm 2.33
	Ir	0.0387	25.50	26.00 \pm 0.03	-	-

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