Determination of Gold in Blister Copper
by Inductively Coupled
Plasma-Atomic Emission Spectrometry*

by Takeshi OBATA

The precise determination of gold has been particularly required on the business transactions of blister copper. Gold is usually analysed by the Fire Assay Gravimetric (FAG) which is main traditional method. However, this method requires special facilities such as the assay crucible furnace and the muffle furnace. These facilities are exclusively used for precious metal determination such as gold. And then, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) which is commonly applied to metal analysis was studied for the determination of gold. Using high dispersive spectrometer, the coexisting elements such as Fe, Ni, Cu, Zn and Sn did not interfere with the determination of Au at the wavelength of 242.795nm. Mn gave positive error, accordingly subtraction from the Au signal was required. As the effect of aqua regia concentration was found, the amount of remained acid was measured at sample decomposition, and the amount of remained aqua regia was estimated. In order to eliminate the matrix effect the concentration of aqua regia and coexist elements between sample and standard solution for calibration were matched.

Analytical results of this proposed method extremely agreed well with that of the FAG method. The discrepancy of the proposed method from the FAG method was less than 3%. The required time for the determination was 8 hrs., including the sampling and dissolution procedures.

KEY WORDS : Blister Copper, Gold, Fire Assay Gravimetric, Inductively Coupled Plasma-Atomic Emission Spectrometry, Manganese

1. Introduction

Determination of gold in blister copper should be analysed with high precision and reliance on the business transactions. Gold in copper materials is usually determined by Fire Assay Gravimetric method (FAG). Since FAG is particularly precise and reliable, it is traditionally used as an official standard. However, this method requires the special facility such as the assay crucible furnace and the muffle furnace which are used for the exclusive use of gold determination and the special skilled assayers to achieve accurate determination. Besides, assayers are forced to work under high temperature environment. On the contrary, Inductively Coupled Plasma-Atomic Emission Spectrometry method is simple and suitable for the routine analysis without special facilities and assayers. This method has been applied to the determination of gold in ores or concentrates. But, some reports were treating rather low concentration range of gold (0-40µg/g) in ores or concentrates and the results were occasionally accompanied with a big error higher than 10%. The present author treated rather higher content gold (200-2800µg/g) in blister copper. These solid phase samples usually involve segregation of ingredients, so that it may result in a big error of the determination especially by using a small quantity of the sample. Therefore, total 5.00g boring chip sample was classified according to their sizes by using sieves was required for the accurate determination.

The interferences of matrix could be eliminated by matrix matching method.

In order to match the concentration of free acid the amount of free acid (HCl and HNO₃) in the decomposed sample and the standard solution for calibration were estimated by calculation and experiment respectively. Analytical results of this proposed method extremely agreed well with that of FAG. The discrepancy of the proposed method from FAG was less than 3%. The time required for the determination was 8 hrs., including the sampling and dissolution procedures.

2. Experiment

2.1 Reagents and Apparatus

a) Hydrochloric acid:
Wako pure reagent for precise analysis, ρ :1.18g/ml, 35% (11.33mol/l)
b) Nitric acid:
Wako pure reagent for precise analysis, ρ :1.38g/ml, 65% (14.2mol/l)
c) Gold, Palladium standard solution:
(1mgAu/ml, 1mgPd/ml)
[99.99% (m/m) up Nippon Mining & Metals Co., Ltd.]
100mg was dissolved with HCl + HNO₃ + H₂O (9 + 3 + 9) 21ml. Fill up 100ml with pure water (0.01mgAu/ml, 0.01mgPd/ml). The freshly prepared solution.
d) Manganese, Iron, Nickel and Zinc standard solution:
(1 mgMn/ml, 1 mgFe/ml, 1 mgNi/ml, 1 mgZn/ml) [99.9% (m/m) up] 100mg was dissolved with HNO₃ + H₂O (1 + 1) 10ml.

Fill up 100ml with pure water.

e) Copper standard solution:
(10 mgCu/ml) [99.99% (m/m) up Nippon Mining & Metals Co., Ltd] 1000mg was dissolved with HNO₃ + H₂O (1 + 1) 20ml. Fill up 100ml with pure water.

f) Tin Standard solution:
(1 mgSn/ml) [99.9% (m/m) up] 100mg was dissolved with HCl + H₂O (1 + 1) 50ml. Fill up 100ml with HCl + H₂O (1 + 1).

g) ICP-AES:
Seiko Instrument Co., Ltd SPS-3000, Grating: 3600/mm.

2・2 Proposed analytical procedure

Boring tip sample (100g) was sieved into three parts by using net sieves of 0.1mm and 1mm. Total 5.00g sample collected in proportion to the mass of each part was taken into a glass beaker, and 45ml of HCl and 15ml of HNO₃ were added, and then allowed to stand at room temperature. After the end of vigorous reaction, the glass beaker was put on a hot plate heated at 130±20°C for 50 min. Since HCl and HNO₃ have the constant boiling mixture with water at 108.5°C and 123°C respectively, the decomposing temperature was selected to be 130±20°C. After cooling, the decomposed sample was transferred into a 100ml volumetric flask. The aliquot of 10ml was taken into a 100ml volumetric flask. Again, add 10ml of the aliquot into a 100ml volumetric flask which previously contained 8.8ml of HCl and 2.9ml of HNO₃. The spectrum intensity of gold at 242.795nm and manganese at 257.610nm were measured by ICP-AES. The intensity of gold was corrected by subtracting the intensity of manganese as described in the following section.

3. Results and discussion

3・1 Effect of the aqua regia content on ICP-AES measurement

As the intensity of ICP-AES was interfered by physical interference such as the viscosity of the sample solution, the effect of aqua regia concentration was studied.

As shown in Table 1, the increase in aqua regia content caused the decrease in the intensity of Au. It seems that the viscosity of the solution increases with increasing aqua regia content and results in the decrease of the nebulizer flow rate. In order to prevent this interference the acid content matching of standard solution was required. The optimum content of aqua regia was 12ml in 100ml as shown in Table 1.

3・2 Estimation of aqua regia in standard and sample solution

In the case of standard solution for calibration the acid amount of HCl and HNO₃ were estimated by calculation as shown in Table 2.

From Table 2, HCl and HNO₃ were 0.5ml and 1.2ml respectively. Optimized aqua regia concentration was 12ml/100ml based on the results in Table 1. Therefore, addition of 8.5ml (= 9 – 0.5) HCl and 1.8ml (= 3 – 1.2) HNO₃ was required.

On the other hand in the case of sample solution the amount of remained acid after dissolving in aqua regia was estimated by titration with 0.98mol/l NaOH. When the blister copper of 5g was taken and dissolved by the proposed procedure, the remaining acid was decreased as the decomposing time was elongated as shown in Table 3.

When the decomposing time was 50min, the consumption...
of 0.98 mol/l NaOH was 4.1 ml and the aliquot used for the titration was 1/100, the remaining amount of HCl and HNO₃ were estimated as follows:

HCl: 0.25 ml \[= 3 \times (0.98 \text{ mol} \times 4.1 \text{ ml} / (11.33 \text{ mol} \times 3 + 14.2 \text{ mol} \times 1))\]

HNO₃: 0.08 ml \[= 1 \times (0.98 \text{ mol} \times 4.1 \text{ ml} / (11.33 \text{ mol} \times 3 + 14.2 \text{ mol} \times 1))\]

Thus, the amount of remaining HCl and HNO₃ were 0.25 ml and 0.08 ml, respectively. Besides, the amount of HCl and HNO₃ to add were 8.8 ml (≈ 9 – 0.25), and 2.9 ml (≈ 3 – 0.08) respectively.

3・3 Effect of coexisting elements on the intensity of Au

The spectral and physical interferences of coexisting elements on the determination of gold at wavelength 242.795 nm was investigated as follows.

3・3・1 Effect of coexisting Fe and Mn on the intensity of Au

The spectra of Fe and Mn appear at the neighbourhood of 242.795 nm. But, the interference of Fe could be avoided by using a high dispersive spectrometer. Mn spectrum was completely overlapped with Au spectrum, as shown in Fig. 1.

The calibration plots for Au and Au containing Mn were shown in Fig. 2, which shows that 1000 µg Mn in 100 ml solution gives positive error of 10 µg Au.

The correction was carried out as follows; the content of Mn was determined by the spectrum at the wavelength of 257.610 nm. The spectrum intensity at 242.795 nm corresponding to the quantity of Mn was evaluated and this value was subtracted from the spectrum intensity at 242.795 nm. Thus, the corrected Au was calculated by the following equation.

Corrected Au (µg/g) = Uncorrected Au (µg/g) – Mn (µg/g) × 10 (µg) / 1000 (µg)

Mn: Found of Mn at 257.610 nm

3・3・2 Effect of coexisting elements (Fe, Ni, Cu, Zn and Sn) on the intensity of Au

Blister copper contained Fe, Ni, Cu,
Zn and Sn, but these elements did not interfere with the measurement at 242.795 nm as shown in Table 4. Recoveries of Au were 97 ~ 101.5% on coexist of Fe, Ni, Cu, Zn or Sn.

3.4 Recovery of gold on the different samples

In order to study the recovery 50 or 100 µg of Au was added to different samples. As shown in Table 5, the recovery was satisfactory in both cases.

3.5 Comparison of analytical results between FAG and the proposed method

As shown in Table 6, the analytical results of this proposed method extremely agreed well with that of the FAG method.

The relative error was less than 3%.

4. Conclusions

Instead of FAG, ICP-AES for the determination of high content (200~2800 µg/g) in blister copper was studied. The increase in aqua regia concentration caused the decrease of the Au signal. On the determination of Au at wavelength 242.795 nm the spectral interference by the coexisting elements were also investigated. It was found that 1000 µg Mn in 100 ml solution gave positive error on 10 µg Au, and coexistence of elements such as Fe, Ni, Cu, Zn and Sn did not interfere with the determination.

Analytical result of this proposed method extremely agreed well with that of the FAG. The relative error was less than 3%. Comparing with the FAG, this method is simple, reliable and reproducible. Even though without special facilities such as assay crucible furnace and muffle furnace which are for the exclusive use of gold determination, the required time was very short.

Acknowledgement The author wishes to express hearty gratitude to Dr. Hideo Imai, Professor at Hiroshima University School of Medicine, for his valuable advice and reading through this manuscript.

References

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6) You Taili, Guangpu Shiyanshi, 14(4)(1997), 80-82.

### Table 5: Recovery of Au on the different samples.

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<th>Recovery %</th>
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### Table 6: Comparison of analytical results between FAG and the proposed method.

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### Table 7: Comparison of analytical results between FAG and the proposed method.

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b Mean of six determinations
d Relative Standard Deviation : (σ/B) x 100%
ICP-AES による粗銅中の金の定量分析

小畑 健

粗銅中の金の取引では、きわめて正確な金の定量分析が要求されており、伝統的な乾式試金法による分析が行われている。しかし、この方法は塩酸融解炉及び吹吹炉など貴金属分析のみを目的に限定された特異な設備を必要とし、また分析操作には長年の熟練を要するという難点がある。そこで、金属分析に汎用的に適用でき、最近広く普及している ICP-AES 法を用いた金の定量分析法を検討した。

高分解能の分光器 ICP-AES を用いた金の波長 242.795nm では、マンガンが共存する場合合金の定量分析を妨害し、正の誤差を与えるため、マンガン量の補正が必要であること。鉄、ニッケル、銅、亜鉛及び錫などの共存元素による妨害は認められないことを明らかにした。

王水濃度の影響が認められたため、試料分解後の酸の残存量を測定して残存王水量を推定し、試料液と検量線用標準液の王水濃度および共存元素濃度とを一致させ、液組成の妨害を回避した。その結果、ICP-AES 法と乾式試金法により得られた分析値は極めてよく一致し、その差は相対的誤差としてわずかに 3% 以下であることが判明した。

分析所要時間はサンプリングおよび分解時間を含めて10時間である。分析操作および結果の詳細を本報告に述べた。

キーワード：粗銅、金の定量分析、乾式試金法、ICP-AES 法、マンガン量の補正。