



## Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Gold

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A solid phase extraction and flame atomic absorption spectrometry for the determination of gold with SEPABEADS SP207 resin as sorbent was studied. The formation of gold complex with 4-rhodanineazo benzoic acid (4-BARA) was preconcentrated on a nonpolar resin SEPABEADS SP207 and pentyl alcohol was used as eluent. The effects of various parameters such as acidity, flow rate of sample, type of eluent, amount of adsorbent and interfering ions have been studied. The gold in 250 mL solution can be concentrated to 5 mL, representing an enrichment factor of 50 was achieved. In the original sample detection limit was  $0.3 \mu\text{g L}^{-1}$  using flame atomic absorption spectrometry. The relative standard deviation for eleven replicate measurements of  $15 \mu\text{g L}^{-1}$  gold was 3.3 %. The method was applied to the determination of trace amount gold in ore samples with good results.

**Key Words:** Solid phase extraction, Gold, 4-Rhodanineazo benzoic acid, Flame atomic absorption spectrometry.

### INTRODUCTION

Gold possesses a unique combination of properties that have resulted in its use in a wide range of industrial applications<sup>1</sup>. Trace level determination of gold by flame atomic absorption spectrometry is difficult like other metal ions due to lower levels of gold than the limit of detection of flame atomic absorption spectrometry and effects of the matrix components of the working media<sup>2,3</sup>. To overcome these limitations on the determination of gold by flame atomic absorption spectrometry, separation-enrichment techniques including solid phase extraction (SPE), cloud point extraction, liquid-liquid extraction, coprecipitation, *etc.*, have been widely applied to the determination of gold<sup>4,5</sup>.

Solid phase extraction method had the advantages of being more sensitive, faster, simple and environment friendly. Solid phase extraction employing on different solid matrices have been successfully used for the preconcentration, separation and sensitive determination of trace metal ions including gold<sup>6-8</sup>.

The aim of this work is to combine solid phase extraction with flame atomic absorption spectrometry and develop a new method for the determination of gold. In this method 4-rhodanineazo benzoic acid (4-BARA), which reacts with Au(III) forming a very stable Au(III)-4-BARA complex. Subsequently, ore samples containing Au(III)-4-BARA complex were passed through SEPABEADS SP207 resin. Gold complexed with 4-BARA were preconcentrated on a nonpolar resin SEPABEADS SP207. The Au(III)-4-BARA complex

adsorbed on SEPABEADS SP207 resin was eluted with pentyl alcohol. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry. The optimum analytical conditions for the quantitative recoveries of gold on SEPABEADS SP207 adsorption resin were investigated.

### EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used to measure the concentration of Au. The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Au 242.8 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

A peristaltic pump mode FIA-3110 (Titan Instruments Co., Ltd. Beijing, China) was used in the solid phase extraction process.

SEPABEADS SP207 resin was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). It is based on crosslinked polystyrenic matrix. SEPABEADS SP207 is widely used in different industrial fields<sup>9</sup>.

4-Rhodanineazo benzoic acid (Fig. 1) was synthesized as reported method<sup>10</sup>. A 0.5 % (w/v) solution of 4-BARA was prepared by dissolving an appropriate amount of 4-BARA in ethanol. All other reagents used were of the highest available purity and of at least analytical reagent grade. Ultra-pure water

of resistivity 18 M $\Omega$  cm obtained from a UPHW purification device (Ulupure Co. Shanghai, China) was used to prepare all the solutions.

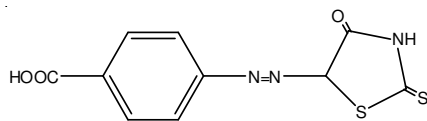


Fig. 1. Structure of 4-rhodanineazo benzoic acid (4-BARA)

All glass and plastic material were thoroughly cleaned and kept into 10 % (m m<sup>-1</sup>) nitric acid for at least 48 h. The material was then rinsed three times with ultra-pure water before being used. Standard stock solutions of Au (1000 mg L<sup>-1</sup>) and the ore reference materials (GBW070021, GBW070022 or GBW070023) were obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution.

**Solid phase extraction:** The stopcock of the glass column (100 mm in length and 10 mm in diameter) was covered with a fritted glass disc. A total of 0.7 g of SEPABEADS SP207 resin was poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the resin beads during sample loading. It was washed successively with methanol, water, 1 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone, water, 1 mol L<sup>-1</sup> NaOH and water, sequentially. The solution containing no more than 50  $\mu$ g of Au(III) in a 250 mL calibrated flask, 5 mL of 0.5 % (w/v) 4-BARA solution was added. The pH was adjusted to the desired value with aqueous ammonia and diluted HNO<sub>3</sub>. The mixture was diluted to the mark and mixed well. The solution was passed through the SEPABEADS SP207 resin column at a flow rate of 10 mL min<sup>-1</sup> (controlled by a peristaltic pump). After the enrichment step was completed, the retained complex was eluted from the resin bed by using 5 mL pentyl alcohol and determined by flame atomic absorption spectrometry. A blank solution was also run under the same conditions without adding gold.

**Sample preparation:** The developed method has been successfully applied to the determination of gold in ore reference materials and ore samples (Tables 1 and 2).

TABLE-1  
DETERMINATION OF GOLD ( $\mu$ g g<sup>-1</sup>) IN THE ORE REFERENCE MATERIALS AFTER APPLICATION OF THE PRESENTED PROCEDURE (n=5)

Ore reference materials	Certified value ( $\mu$ g g <sup>-1</sup> )	Present value ( $\mu$ g g <sup>-1</sup> )
GBW070021	1.43 $\pm$ 0.10	1.41 $\pm$ 0.14
GBW070022	2.36 $\pm$ 0.13	2.33 $\pm$ 0.20
GBW070023	3.60 $\pm$ 0.12	3.56 $\pm$ 0.16

TABLE-2  
DETERMINATION OF Au ( $\mu$ g g<sup>-1</sup>) IN ORE SAMPLES (n=5)

Samples	Added	Found <sup>a</sup> by present method	Recovery (%)
Ore 1	0	5.8 $\pm$ 0.1	-
	5	10.5 $\pm$ 0.2	94.0
	10	16.0 $\pm$ 0.3	102
Ore 2	0	6.2 $\pm$ 0.1	-
	5	11.4 $\pm$ 0.2	104
	10	15.9 $\pm$ 0.3	97.0

- not determined; <sup>a</sup> Mean  $\pm$  S.D

The 10 g of ore reference materials or ore samples were transferred into a porcelain crucible and roasted for 3 h in a muffle furnace at 650  $^{\circ}$ C. After roasting, the samples were transferred to 1000 mL beaker and 120 mL freshly prepared aqua regia was added to sample. 2.0 g of NaCl was added to stabilize the gold chloride complex during evaporation on a hot plate. The beaker was covered with a watch glass and heated on a hot plate. Heating was continued for at least 6 h and more aqua regia was added at regular intervals to maintain the free acid level at *ca.* 1 cm above the sample level. The watch glasses were then removed and the content was evaporated slowly until the residue became nearly dry. Then 40 mL of 6 mol L<sup>-1</sup> HCl was added to the beaker and the mixture was heated to dryness. This last step was repeated twice to ensure total elimination of HNO<sub>3</sub>. The residue was diluted with 0.1 mol L<sup>-1</sup> HCl solutions. Afterwards, sample solution was cooled and filtered using the filter paper. The residue was washed with minimum amounts of 0.1 mol L<sup>-1</sup> HCl. The filtrate was collected into a 100 mL of calibrated flask quantitatively and the gold contents were analyzed according to the general procedure. The ore samples were collected from Jin Bao Mountain (Dali, P.R. China).

**Flame atomic absorption spectrometry analysis:** The flame atomic absorption spectrometry analysis condition is listed in Table-3. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated 3 times and the obtained signals were averaged.

TABLE-3  
SETTING OF ANALYTICAL CONDITIONS

Analytical condition	Gold
Calculation mode	Integral
Wavelength (nm)	242.8
Slit width (nm)	1.3
Lamp current (mA)	10
Burner height (mm)	7.5
Fuel gas flow rate (L min <sup>-1</sup> )	1.8

## RESULTS AND DISCUSSION

**Effect of pH:** The acidity of the sample solution is one of the important factors affecting the formation of Au(III)-complex and the subsequent solid phase extraction. According to the results (Fig. 2), quantitative recoveries (> 95 %) for analytes were obtained. The optimum pH range is 3-5. The pH was adjusted to the desired value with aqueous ammonia and diluted HNO<sub>3</sub>. Therefore, to obtain the maximum extraction efficiency, pH of the sample solution should be carefully adjusted at pH 4.

**Influences of ligand amount:** In order to determine the amounts of 4-BARA required for quantitative recovery for Au(III), the proposed method was applied. For up to 50  $\mu$ g of Au(III), the use of about 3-6 mL of 0.5 % (v/v) 4-BARA solution was found to be sufficient for complete reaction. Accordingly, 5 mL of 4-BARA solution is enough for the separation and preconcentration procedure because of the low level of the investigated Au(III) concentrations in real samples.

**Effects of the amount of resin:** The amounts of solid phase extraction material are also another important factor on

the column studies for the quantitative recoveries of metal complexes. The effect of the amount of SEPABEADS SP207 resin on the sorption of metal ions was examined in the range of 0.4-1.0 g. The results demonstrated that, quantitative recoveries (> 95 %) of gold was observed in the range of 0.6-0.8 g. Above 0.8 g the recoveries were below 95 % with 5 mL of the eluent. Therefore, in the proposed procedure, 0.7 g of SEPABEADS SP207 resin is recommended.

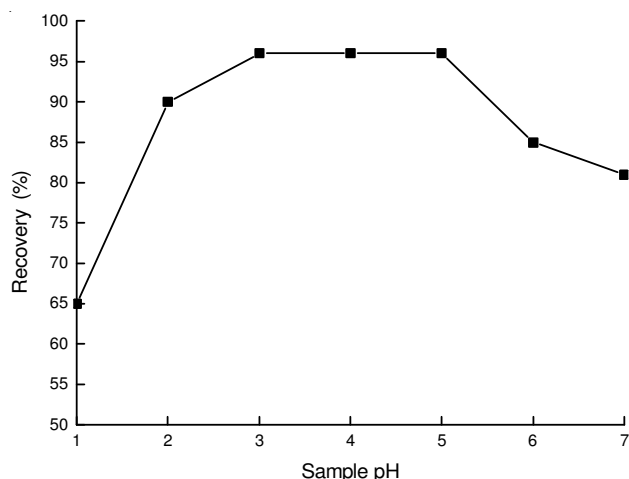


Fig. 2. Influences of acidity on the recovery of gold; Conditions: sample volume: 250 mL; flow rate: 10 mL min<sup>-1</sup>; amount of the resin: 0.7 g

**Effect of flow rate of sample solution and eluent:** The influence of flow rate on the adsorption of Au(III)-4-BARA complex was also studied. Flow rate in the range of 5-15 mL min<sup>-1</sup> had no significant effect on the recoveries of Au(III). Therefore, in the proposed procedure, 10 mL min<sup>-1</sup> flow rate is recommended.

Among several media investigated as eluent (pentyl alcohol, methanol, acetone, ethanol, ethyl acetate, 2-methoxyethanol), only pentyl alcohol showed satisfactory elution characteristics. 5 mL of pentyl alcohol provided quantitative recovery (> 95 %) and reproducibility. The flow rate of eluent solution was examined in the range of 0.5-5.0 mL min<sup>-1</sup>. Maximum recoveries for gold was obtained in the range of 0.5-3 mL min<sup>-1</sup>. The flow rate of 2 mL min<sup>-1</sup> was chosen as optimum value.

**Loading capacity:** To 0.1 g resin was placed in the conical flasks. Stock solution of Au(III) and 4-BARA were added to the flask. Acidity of the solution was adjusted to pH 4 using aqueous ammonia and diluted HNO<sub>3</sub>. After shaking for 4 h, the mixture was filtered. Concentration of Au(III) was measured by flame atomic absorption spectrometry. The loading capacity of SEPABEADS SP207 resin was 10 mg g<sup>-1</sup> for gold.

**Maximum sample volume and enrichment factor:** The enrichment factor was studied following recommended column procedure by increasing volume of Au(III) solution and keeping the total amount of loaded Au(III) constant to 50 µg. For this purpose, 50, 100, 150, 250, 300 and 350 mL of sample solutions containing 50 µg Au(III) were passed through the column at the optimum flow rate. The results showed that the maximum sample volume could be up to 250 mL with the recovery > 95 %. Therefore, 250 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. And a high enrichment factor of 50 was obtained.

**Limit of detection:** Using the optimized conditions of preconcentration, calibration curve was prepared for Au(III). The limit of detection (LOD) value (blank + 3 s)<sup>11</sup>, where s is standard deviation of blank determination (n = 11), were found to be 0.3 µg L<sup>-1</sup>. The relative standard deviation for eleven replicate measurements of 15 µg L<sup>-1</sup> gold was 3.3 %. SEPABEADS SP207 resin can be reused at least 50 times.

**Effect of neutral electrolytes and coexisting metal ions:** Various neutral electrolytes, viz. NaCl, KNO<sub>3</sub>, MgSO<sub>4</sub>, CaCl<sub>2</sub> and KCl at 0.1 mol L<sup>-1</sup> level and 600 µg of coexisting metal ions, viz. Pd, Pt, Ag, Fe, Co, Ni and Cu do not have any deleterious effect on the enrichment of 50 µg gold present in 250 mL of aqueous solution during enrichment with 0.7 g of SEPABEADS SP207 resin.

**Applications of the presented procedure:** In order to establish the validity of the proposed procedure, the method has been applied to the determination of Au in the ore reference materials samples. The results were given in Table-1.

The proposed method was applied to determine gold in the ore samples. The results for the ore samples were given in Table-2. The results indicate that the recoveries in the range of 94.0-104 % are reasonable well for trace analysis.

## Conclusion

A new method of solid phase extraction combined with flame atomic absorption spectrometry has been proposed for the determination of gold in ore sample. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of SEPABEADS SP207 resin was as high as greater than 50 cycles without any loss in its sorption behaviour. The tolerance limits of interfering ions on the recovery of gold ions are quite high. The results acquired from the analyses of the certified reference samples confirmed the reliability of the method. The method suitable for the determination of trace amount of gold in ore samples.

## ACKNOWLEDGEMENTS

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