

Flame Atomic Absorption Spectrometric Determination of Gold by Solid Phase Extraction Using Modified Nanometer Titanium Dioxide as Sorbent

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The nanometer titanium dioxide immobilized on silica gel (NTDS) loaded with 5-(2-hydroxy-5-nitrophenylazo)-thiorhodanine (HNATR) was prepared and its solid phase extraction of gold was investigated. Gold could be adsorbed quantitatively when the gold-bearing samples flew through the column in 1.0 mol/L in phosphoric acid medium. The gold enriched on the column was eluted with 0.1 mol/L of sodium thiosulfate, realizing the high enrichment factor of low concentration gold and the separation of most interfering ions. Gold in the eluant was measured by flame atomic absorption spectrometry. Under the chosen experimental conditions, Beer's law was obeyed in the range of 0.05-3.0 µg/mL for Au(III) with the correlation coefficient (*r*) of 0.9996. This method was used to determination of gold in ore and environmental waste samples with RSD in the range of 2.2-3.2 % and addition recovery of 88-104 %.

Key Words: Flame atomic absorption spectrometry, Gold(III), Solid phase extraction, Nanometer titanium dioxide immobilized on silica gel, 5-(2-Hydroxy-5-nitrophenylazo)-thiorhodanine.

INTRODUCTION

There are many methods for the determination of gold in literature. Since the concentration of gold in ores and environmental samples is low, it is difficult to measure directly and the gold should be pre-enriched before analysis. The common methods include solvent extraction, active carbon adsorption, ion-exchange enrichment and foam plastic adsorption. However, most of these methods have long measuring steps and low enrichment factor¹⁻⁴.

In recent years, the solid phase extraction has been extensively used in analytical chemistry due to its high enrichment factor, little environmental pollution, difficult emulsified and time-saving⁵⁻⁷. At present, reverse phase bond silica, polymer material and ion exchange resin have been widely used in the pretreatment of gold samples^{5,8,9}.

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The nanocomposite materials also received more and more attentions in recent years^{10,11}. Nanoparticulate metal oxides exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances, such as acidic gases and organics¹². The previous studies show that nanometer TiO₂ material is a promising solid-phase extraction adsorbent for metal ions¹³⁻¹⁶. 5-(2-Hydroxy-5-nitrophenylazo)-thiorhodanine (HNATR) was synthesized and used in the photometric analysis of gold in our previous studies. The results showed that this compound had high sensitivity and selectivity in the determination of gold⁶. Our subsequent investigation indicated that HNATR could adhere stably on nanometer titanium dioxide immobilized on silica gel (NTDS) and it could not be eluted away by water medium. The NTDS loaded HNATR was prepared in this study. After separated and enriched by solid phase extraction column with this material, gold(III) was determined by flame atomic absorption spectrometry with reproducible results.

EXPERIMENTAL

Spectr AA 200 atomic absorption spectrophotometer (Varian Technologies China, US), KY-2 gold hollow cathode lamp (Beijing ShuGuang Ming Electronic Lighting Instrument Co., Ltd.). All solutions were prepared using deionized water from a Nanopure water system (Millipore corporation, USA). Gold standard stock solution: 1.0 mg/mL, which was purchased from National Standard Substance Research Center. The solution was gradually diluted to standard working solution at 0.2 µg/mL when used. The NTDS was prepared by sol-gel method in our laboratory according to previously reported literature¹⁷. HNATR solution, 1.0 % (m/v), was prepared by dissolving 0.25 g of the reagent in 25 mL ethanol.

Preparation of modified NTDS cartridge: In a 50 mL beaker, 10.0 g of NTDS was added to 10 mL of HNATR ethanol solution (1.0 %) and mixed well. The ethanol was evaporated and the modified NTDS was obtained. A Teflon cartridge (0.6 cm length and 0.3 mm in diameter, Fig. 1) was packed with 0.2 g of the modified NTDS.

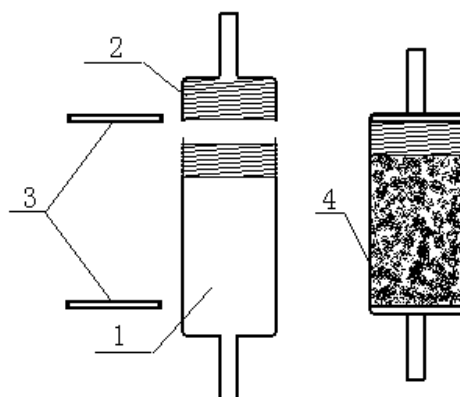


Fig. 1. NTDS loaded HNATR cartridge (1) Tube for fill in sorbent, (2) Screw cap for sealing the tube, (3) Sieve plate, (4) NTDS loaded HNATR

AAS parameter: The analysis line wavelength of gold was 242.8 nm. The current of hollow cathode lamp was 4.0 mA and the flow rate of air was 6.0 L/min. The flow rate of acetylene was 1.8 L/min and the spectrum band width was 0.5 nm. The burner height was 12.5 mm and the measurement mode was integration while the measuring time was 10 s.

Analysis procedure: A proper volume of standard samples or samples (total content of gold < 6.0 mg) was flown through the NTDS loaded HNATR column at the rate of 10 mL/min for the solid phase extraction followed. The enriched gold on column was eluted reversely with 2.0 mL of 0.1 mol/L of sodium thiosulfate. The eluant was collected into 2.0 mL calibration tube, diluted accurately to constant volume and measured by atomic absorption method.

RESULTS AND DISCUSSION

Selection of column medium: The effects of column mediums on the extraction rate of gold were investigated. The results showed that gold could be well adsorbed in NTDS loaded with HNATR column in acidic mediums and phosphoric acid solution had the best efficiency. The effect of phosphoric acid concentration on gold recovery was investigated. Gold(III) solution at 0.2 µg/mL was flown through the column with different concentrations of phosphoric acid medium. As the results shown in Fig. 2, when the concentration of phosphoric acid was in the range of 0.5-4.0 mol/L, Au(III) could be well adsorbed in the NTDS solid phase extraction column loaded HNATR. The gold extraction ratio was above 95 %. Therefore the medium in this study was 1.0 mol/L of phosphoric acid.

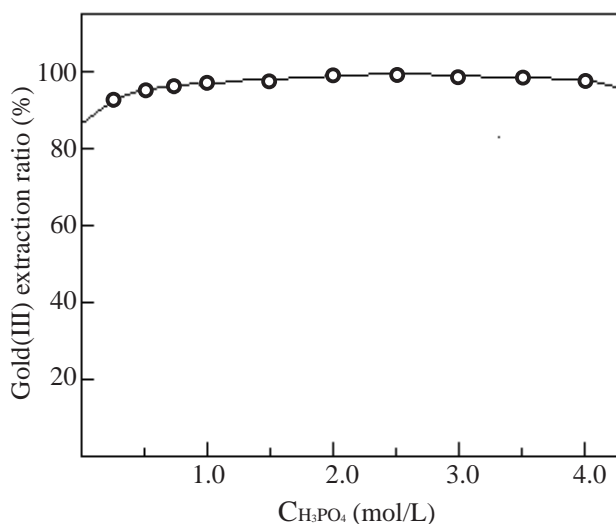


Fig. 2. Effect of H₃PO₄ concentration on Au(III) extraction ratio

Determination of extraction capacity: 5.0 µg/mL of Au(III) solution was prepared to determine the extraction capacity of column. The results showed that gold began leaking when the column volume was more than 1.2 L, indicating that maximum enrichment amount of gold by column was 6.0 mg. Under the chosen experimental conditions, the gold content in samples was at the microgram grade and would not exceed the column extraction capacity. When the sample volume was 20 L, the recovery rate of gold was above 94 % for Au(III) at 0.01 µg/mL. Therefore, this method was suitable for the enrichment of Au(III) at low concentration and the enrichment factor was high.

Selection and dosage of eluant: The samples were eluted with eluant after enrichment. The effects of eluants including thiourea, nitric acid, EDTA and sodium thiosulfate on the eluting of gold were studied. As the results shown in Table-1, thiourea and sodium thiosulfate solution could elute gold completely when the enrichment amount of gold was 50 µg. However, sodium thiosulfate had better eluting effect. Therefore, 0.1 mol/L of sodium thiosulfate was used as eluant in this study.

TABLE-1
EFFECT OF DIFFERENT ELUANT ON THE RECOVERY (%) OF GOLD

Eluant	Volume (mol/L)	Recovery (%)					
		0.6 mL	1.0 mL	1.5 mL	2.0 mL	2.5 mL	3.0 mL
HNO ₃	0.02	15.2	28.6	39.8	46.7	52.80	59.4
	0.10	17.2	34.3	46.7	54.4	61.60	69.2
	0.50	22.8	43.9	62.7	75.05	88.20	92.1
Thiourea	0.02	36.8	60.2	80.5	92.1	96.20	97.5
	0.10	45.2	70.5	89.2	95.8	98.20	98.9
	0.50	48.9	76.6	92.8	97.4	98.60	99.2
EDTA	0.02	6.82	11.8	13.6	16.8	22.50	24.8
	0.10	8.02	12.7	15.4	19.6	25.10	27.6
	0.50	11.2	16.9	21.7	28.7	36.75	41.2
Na ₂ S ₂ O ₃	0.02	63.4	93.6	98.5	99.4	–	–
	0.10	67.4	95.2	99.1	99.6	–	–
	0.50	69.5	96.3	98.6	99.2	–	–

The elution of gold in the reversed direction after enrichment could shorten the elution distance, reduce eluant dosage and increase enrichment factor. When enrichment amount of gold was 50 mg in column, 5.0 mL of eluant could elute the gold completely in positive direction, while it only needed 1.8 mL of eluant in the reversed direction after enrichment. Therefore, the enriched gold on the column was eluted reversely with 2.0 mL of eluant.

Working curve: Under the experimental conditions, Beer's law was obeyed in the range of 0.05-3.0 µg/mL for Au(III). The regression equation was $A = 0.264 C$ (µg/mL) + 0.0142 with the correlation coefficient of $r = 0.9996$.

Effect of concurrent ions: For determining 2.0 mg of Au(III) with the relative error below $\pm 5\%$, the following ions had no interference on measurements (mg): NH₄⁺, Na⁺, Cl⁻, PO₄³⁻, SO₄²⁻ (100); Ca²⁺, Mg²⁺, Al³⁺ (50); Cr³⁺, Mo⁶⁺, W⁶⁺, Ti⁴⁺, Pd²⁺, Sb³⁺ (20); Pb²⁺, Cd²⁺, Mn²⁺, Ag⁺, Sn⁴⁺ (10); Ni²⁺, Hg²⁺, Pt⁴⁺, Cu²⁺ (5); Pd²⁺, Rh³⁺, Ru³⁺, Ir⁴⁺, Co²⁺, Fe³⁺, Zn²⁺ (2). The selectivity of this method is high.

Samples analyses: 1-10 g of ore samples were weighed into a porcelain crucibles according to the content of gold. The samples were roasted for 2-4 h at 600-700 °C. Then they were transferred into 400 mL beaker after cooling. After the sample was infiltrated with water, 50 mL of aqua regia was added. The samples were heated by electric hot plate to almost dry and then 10 mL of 1% (m/v) animal glue solution was added immediately under vigorous stirring. After 100 mL of 1.0 mol/L phosphoric acid was added, the solution was stirred, clarified and filtered. The filtrate was flown through NTDS column loaded HNATR at the rate of 10 mL/min. The enriched gold was eluted with 0.1 mol/L of sodium thiosulfate. The solution was analyzed according to experimental method with blank reagent as reference and the results are shown in Table-2.

TABLE-2
DETERMINATION RESULTS OF SAMPLES

(Samples	Found (µg/g)	Standard value (µg/g)	RSD % (n = 5)	Recovery % (Au ³⁺ , 2.0 µg)
GBW(E) 070012	0.297	0.30 ± 0.02	2.4	94~101
GBW(E) 070014	3.180	3.14 ± 0.06	3.2	96~103
GBW(E) 070015	9.940	10.0 ± 0.20	2.6	95~99
Electroplating wastewater	15.60 (µg/L)	19.5 (µg/L)*	2.8	93~104
Smeltery wastewater	6.74 (µg/L)	6.82 (µg/L)*	2.2	88~97

*Determination results of ICP-MS method.

100 mL of electroplating wastewater or 500 mL of smeltery wastewater were sampled. The samples were acidized with nitric acid. The solution was filtered to remove suspension and residue and then adjusted with phosphoric acid to the concentration of 1.0 mol/L. Then the solution was flown through NTDS column loaded HNATR at the rate of 10 mL/min. The enriched gold on the column was eluted with 0.1 mol/L of sodium thiosulfate. The solution was analyzed according to experimental method with blank reagent as reference and the results are shown in Table-2.

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