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Study on the Solid Phase Extraction and Spectrophotometric Determination of Gold with 5-(2-Hydroxy-4-nitrophenylazo)thiorhodanine

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In this paper, a new chromogenic reagent, 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine (HNATR) was synthesized. A highly sensitive, selective and rapid method for the determination of gold based on the rapid reaction of gold with HNATR and the solid phase extraction of the coloured chelate with a reversed phase polymer-based C_{18} cartridge has been developed. In the presence of 0.05–0.5 mol L^{-1} of hydrochloric acid solution and emulsifier-OP medium, HNATR reacts with gold to form a red chelate of molar ratio 1 : 2 (gold : HNATR). This chelate was enriched by solid phase extraction with a polymer-based C_{18} cartridge and eluted form the chelate from cartridge with dimethyl formamide (DMF). The enrichment factor of 100 was achieved. In the DMF medium, the molar absorptivity of the chelate is 1.23×10^5 L $mol^{-1}cm^{-1}$ at 550 nm. Beer's law is obeyed in the range of 0.01–3 μg mL^{-1} in the measured solution. The relative standard deviation for eleven replicate sample of 0.5 μg L^{-1} level is 2.18%. The detection limit, based on the three times of standard deviation is 0.02 μg L^{-1} in the original sample. This method was applied to the determination of gold in water and ore with good results.

Key Words: Gold, Solid phase extraction, Spectrophotometry, 5-(2-Hydroxy-4-nitrophenylazo)thiorhodanine.

INTRODUCTION

Gold belongs to the elements which occur on Earth with very low natural content. It is one of the most important noble metals due to its wide application in industry and economic activity. For this reason, a simple, sensitive and selective method for determination of trace gold was required strongly. Although several sophisticated techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), electrochemical spectrofluorimetry, neutron activation analysis and the like have widely been applied to the determination of gold[1-9], but the spectrophotometric

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method still has the advantage that it is simple and does not need expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric methods for the determination of gold have been reported; each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity[10–18]. However, the routine spectrophotometric methods are often not sensitive enough to determine the low concentration of gold ion in water or ore samples, the gold concentration of only μg L^{-1} or ng L^{-1} level. For the determination of low concentration of gold ions, a preconcentration step is usually required.

Solid phase extraction is an attractive technique because of its notable advantages. In our previous works, the determination of some trace metal ions by solid phase extraction with reserved phase silica-bond with C_{18} cartridge was studied[19–23]. However, the routine reserved phase silica-bond C_{18} cartridge can be used only in the pH range 2–8. The chromogenic systems in acidic or alkaline medium cannot be preconcentrated by this cartridge. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, in this paper, the colour reaction of 5-(*p*-aminobenzylidene)thiorhodanine (HNATR) with gold and the solid phase extraction of Au-HNATR chelate with a reversed phase polymer-based C_{18} cartridge has been studied. The polymer-based C_{18} is manufactured from a hydrophilic methacrylate polymer, which is functionalized with C_{18} ligands. It is a reversed-phase solid phase cartridge that provides a broad range of solvent choices and a pH range from 0–14. By using the polymer-based C_{18} cartridge, the Au-HNATR chelate was enriched by solid phase extraction in hydrochloric acid medium and the enrichment fact of 100 was achieved. Based on this, a highly sensitive, selective and rapid method for the determination of gold in water and ore samples was developed.

EXPERIMENTAL

A UV-160A spectrophotometer (Shimadzu Corporation, Tokyo, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ-200 pH-meter (Beckman Instruments, Fullerton, USA). The extraction was performed on Waters solid phase extraction (SPE) device (it can prepare twenty samples simultaneously) and a reversed phase polymer $C18^{TH}$ polymer-based C_{18} cartridge (Beijing Genosys Technologies, P.R. China) was used.

Synthesis of HNATR: In a 100 mL beaker, 1.54 g of 4-nitro-2-aminophenol was dissolved in 45 mL of 95% alcohol. To this solution, 12.0 mL of 6.0 mol L^{-1} HCl was added and then the solution cooled to 0°C. After this, 7.0 mL of 10% $NaNO_2$ was added slowly with stirring to obtain a diazotized salt. In another 200 mL beaker, 1.78 g of thiorhodanine and 14 mL of 7.5 mol L^{-1} ammonia were added. After the solution had been cooled to 0°C, the above diazotized solution was added dropwise and the mixture left overnight. The solution was then acidified to pH 1 with concentrated HCl and the precipitate was isolated by filter. The crude product was recrystallized with 90% ethanol 3 times and pure HNATR was obtained with a 68% yield. Its structure was verified by IR, ^1H NMR, MS spectrometry and elemental analysis. Elemental analysis: $C_9H_6N_4O_3S_3$, calcd. (found) (%): C 34.39 (34.25), H 1.92 (2.08), N 17.82 (17.62), S 30.60 (30.52). IR (KBr) (cm^{-1}): 3600 ν(—OH), 3275 ν(—N—H); 3050, 3050 ν(═C—H); 1545, 1360 ν(—N═O); 1645 δ(N—H); 1540, 1505, 1440 ν(C═C); 1290 ν(C—N); 1150, 1225 ν(C═S); 1210 δ(C═S); 825 δ(Ar-H); 805 δ(C═C—H). ^1H NMR (solvent: acetone-d_6) (δ, ppm): 4.82 (1H, s, O—H, H 1); 7.65 (1H, s, Ar-H, H 2); 7.74 (1H, d, Ar-H, H 3); 7.22 (1H, d, Ar-H, H 4); 2.58 (1H, s, —C—H, s, H 5). MS (EI) (m/z): 314 (M^+). All these show that the HNATR has the following structure (Fig. 1).

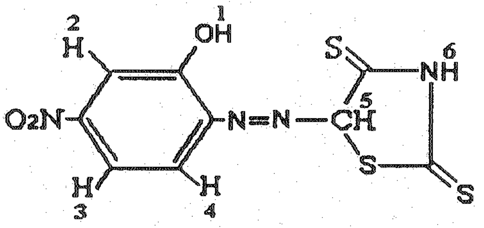

Fig. 1. Structure of 5-(2-hydroxy-4-nitrophenylazo)thiorhodanine (HNATR)

All chemicals used were of analytical grade unless otherwise stated. All solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP reagent water system (Millipore Corporation, USA). High purity dimethyl formamide (DMF) (Fisher Corporation, USA) was used. HNATR solution (3.0×10^{-4} mol L^{-1}) was prepared by dissolving HNATR in DMF. A stock standard solution of gold (1.0 mg mL^{-1}) was obtained from Chinese Material Standard Center and a work solution of 0.5 μg mL^{-1} was prepared by diluting this solution. 5 mol L^{-1} of hydrochloric acid was used. Emulsifier-OP solution (2.0% (v/v)) was prepared by dissolving emulsifier-OP with water.

General Procedure

To a standard or sample solution containing no more than 3.0 μg of Au(III) in a 100 mL of calibrated flask, 5 mL of hydrochloric acid solution (5 mol L^{-1}), 5.0

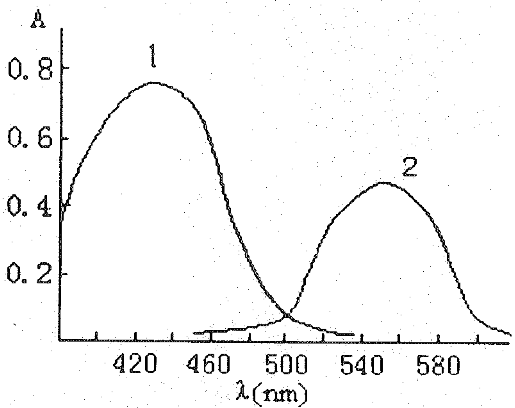

Fig. 2. Absorption spectra of ABTR and its Au (III) complex: ^{1}H NAR-emulsifier-OP blank against water. ^{2}H NAR-emuslifier-OP-Au(III) chelate against reagent blank

mL of HNATR solution (3.0×10^{-4} mol L^{-1}) and 3.0 mL of emulsifier-OP (2.0%) solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 10 min, the solution was passed through the polymer-based C_{18} cartridge at a flow rate of 20 mL min^{-1}. After the enrichment was finished, the retained chelate was eluted from the cartridge at a flow rate of 5 mL min^{-1} with 1.0 mL of DMF in the reverse direction. The eluent was adjusted to the accurate volume of 1.0 mL in a 1.0 mL calibrated flask by adding micro amount of DMF with a 200 μL syringe. The absorbance of this solution was measured at 550 nm in a 1 cm microcell (0.5 mL) against a reagent blank prepared in a similar way without gold.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of HNATR and its Au(III) chelate are shown in Fig. 2. The absorption peaks of HNATR and its complex in DMF medium are located at 430 and 550 nm, respectively.

Effect of acidity: Results showed that the optimal condition for the reaction of Au(III) with HNATR is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid and the like, on the color reaction of Au(III) with HNATR was studied. Experiment shows that hydrochloric acid has the best effect, and the concentration of hydrochloric acid within a 0.05–0.5 mol L^{-1} was found to give a maximum and constant absorbance, so 5 mL of hydrochloric acid was recommended.

Effect of surfactants: The effects of surfactants on Au(III)-HNATR system were studied. The results (Table-1) showed that in the absence of surfactants, anionic surfactants or cationic surfactants, the Au(III)-HNATR chromogenic system give a low absorption, whereas in the presence of non-ionic surfactants, the absorption of the chromogenic system increases markedly. Various anionic surfactants enhance the absorbance in the following sequence: Emulsifier-OP > Tween-80 > Tween-20 > Tween-60. Accordingly, the emulsifier-OP was the best additive, and the use of 1.5–4 mL of emulsifier-OP solution gave a constant and maximum absorbance. Consequently, the use of 3.0 mL was recommended.

TABLE-1

THE EFFECT OF SURFACTANTS ON Au(III)-HNATR CHROMOGENIC SYSTEM

Surfactant	Absence	Emulsifier-OP	Tween-80	Tween-20	Tween-60	SDS	CTMAB	CPB
λ_{max}	530	550	545	540	535	530	535	525
ε ($\times 10^4$) L mol^{-1} cm^{-1}	8.26	12.3	9.18	10.2	8.36	7.18	5.84	6.85

Effect of HNATR concentration: For up to 3.0 μg of Au(III), the use of 5 mL of HNATR solution (3.0×10^{-4} mol L^{-1}) was found to be sufficient for a complete reaction. Accordingly, 5.0 mL of HNATR solution were added in all further measurement.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 8 min at room temperature and remains stable for at least 5 h. After having been extracted into the DMF medium, the chelate was stable for at least 8 h.

Solid Phase Extraction: Both the enrichment and the elution were carried out on a Waters SPE device (which can prepare twenty samples simultaneously). The flow rate was set to 20 mL min^{-1} during enrichment and 5 mL min^{-1} during elution.

Some experiments were carried out in order to investigate the retention of HNATR and its Au(III) chelate on the cartridge. It was found that the HNATR and its Au(III) chelate was retained on the cartridge quantitatively when they pass the cartridge as hydrochloric acid medium. The capacity of the cartridge was determined as 22 mg for Au(III)-HNATR chelate in a 100 mL of solution. In this experiment, the maximum amount gold is only 3.0 μg. Therefore, the cartridge has adequate capacity to enrich the Au(III)-HNATR chelate.

In order to choose a proper eluant for the retained HNATR and its Au(III) chelate, various organic solvents were studied. For eluting the Au(III)-HNATR chelates from the cartridge, the volume of the solvent needed is 0.8 mL for DMF, 1.2 mL for isopentyl alcohol, 1.4 mL for acetone, 1.4 mL for acetonitrile, 1.8 mL for ethanol and 2.0 mL for methanol. The maximal enrichment was achieved when DMF was selected as eluant. So, the DMF was selected as eluant. The experiment show that it was easier to elute the retained HNATR and its Au(III) chelate in reverse direction than in the forward direction, so that it is necessary to upturn cartridge when elution. 1.0 mL of DMF was sufficient to elute the HNATR and its Au(III) chelate from cartridge at a flow rate of 5 mL min^{-1}. The volume of 1.0 mL was selected.

Calibration curve and sensitivity

The calibration curve showed that Beer's law is obeyed in the concentration range of 0.01–3 μg Au(III) per mL in the measured solution. The linear regression equation obtained was $A = 0.621\ C\ (\mu g\ mL^{-1}) + 0.0154\ (r = 0.9992)$. The molar absorptivity was calculated to be 1.23×10^5 L mol^{-1} cm^{-1} at 550 nm. The relative standard deviation at a concentration level of 0.5 μg L^{-1} of Au(III) (11 repeats determination) was 2.18%. The detection limit, based on the three times of standard deviation is 0.02 μg L^{-1} in the original sample.

Interference

The selectivity of the proposed method was investigated by the determination of 0.5 μg to 100 mL^{-1} of Au(III) in the presence of various ions within a relative error of ±5% are given in Table-2. The result shows that most common ions do not interfere with the determination. This method is highly selective.

Composition of the complex: The composition of the complex was determined by continuous variation and molar ratio method. Both showed that the molar ratio of Au(III) to HNATR is 1:3.

Application

Water samples: For water sample, the samples were acidified with hydrochloric acid and filtered by 0.45 μm filter. The gold contents were analyzed according to general procedure. The results (deducted the reagents blank) are shown in Table-2. An ICP-MS method was used as a reference method and the results are shown in Table-2.

TABLE-2
TOLERANCE LIMITS FOR THE DETERMINATION OF 1.0 μg of Au(III) WITH HNATR (Relative error ± 5%)

Ions added	Tolerate (mg)
NO_3^-, K^+, borate, Na^+	50
Li^+, Al^{3+}, PO_4^{3-}, NO_2^-, SO_4^{2-}, ClO_4^-	20
Ca^{2+}, Mg^{2+}, SO_3^{2-}, Sr^{2+}, Ba^{2+}, IO_3^-, BrO_3^-, ClO_3^-	10
Mn^{2+}, Ce(IV), W(VI), Mo(VI), U(IV), Fe^{3+}	4
Ti(IV), Bi(III), V(V), Cr(VI), Zr(IV), F^-, Fe^{2-}, Cl^-	1
Cd^{2+}, Cr^{3+}, La^{3+}, Sn(IV), Zn^{2+}, Zr(IV), Co^{2+}, Ni^{2+}	0.5
Ru(III), Bi(III), Pb^{2+}, Sb^{3+}, Th(IV), Br^-, Os(VIII), I^-, Cu^{2+}	0.2
Se(IV), Te(IV), $S_2O_3^{2-}$, Ag^+	0.1
Ir(IV) , Rh(III), Ru(III)	0.05
Pt(IV), Hg^{2+}	0.01
CN^-, SCN^-	0.005

Ore samples: 1.0 g of ore sample is weighed into 50 mL of teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China) to which 10 mL of aqua regia was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 30 min. The digested material was evaporated to incipient dryness. Then, 20 mL of hydrochloric acid (5%) was added and heated close to boiling to leach the residue. After cooling, the residue was filtered and the undissolved residue was washed with hydrochloric acid (5%) two times. The leachate was collected in a 100 mL calibrated flask quantitatively and the gold contents were analyzed according to general procedure. The results (deducted the reagents blank) are also shown in Table-2. An ICP-MS method as was used as a reference method and the result are also shown in Table-3.

TABLE-3
DETERMINATION OF GOLD IN THE WATER AND ORE SAMPLES

Samples	ICP-MS method	Found	RSD% (n = 5)	Recovery (%) (n = 5)
River water	4.86 (μg L^{-1})	4.67(μg L^{-1})	3.6	89
Planting effluents	31.6 (μg L^{-1})	32.9 (μg L^{-1})	2.8	94
Ore GBW(E)070012	0.358 (g T^{-1})	0.389 (g T^{-1})	3.4	92
Ore GBW(E)070014	3.62 (g T^{-1})	3.56 (g T^{-1})	3.1	95

Conclusion

This method has high selectivity and high sensitivity. 5-(2-Hydroxy-4-

nitrophenylazo)thiorhodanine is a sensitive and selective spectrophotometric reagent for gold. The molar absorptivity of the chelate reaches 1.23 × 105 L mol^{-1} cm^{-1}. Most foreign ions do not interfere with the determination. By solid phase extraction with C_{18} cartridge, the HNATR-Au(III)) chelate in 100 mL solution can be concentrated to 1.0 mL. The enrichment fact of 100 was achieved. The detection limit reached 0.02 μg L^{-1} in the original samples and μg L^{-1} level of gold can be determined with good results.

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