Solid Phase Extraction and Spectrophotometric Determination of Gold with 5-(2-Hydroxy-4-nitrophenylazo)-rhodanine as Chromogenic Reagent

Yinhai Ma[a,b], Yongfang Peng[a,b], Liya Zhu[b], Jiayuan Yin[b*], Qiufen Hu[b] and Jing Chen[b]

[a]*Department of Chemistry, Kunming Teachers' College, Kunming 653100, P.R. China.*
[b]*Department of Chemistry, Yunnan University, Kunming, 650091, P.R. China.*

Received 15 April 2005; revised 11 July 2005; accepted 22 July 2005.

ABSTRACT

This paper presents the synthesis and application of 5-(2-hydroxy-4-nitrophenylazo)-rhodanine (HNAR) as a new chromogenic reagent for the determination of gold. Based on the rapid reaction of gold with HNAR and the solid phase extraction of the coloured chelate with a reversed phase polymer-based C_{18} cartridge, a highly sensitive, selective and rapid method for the determination of gold has been developed. In the presence of 0.05–0.5 mol L^{-1} of phosphoric acid solution and emulsifier-OP medium, HNAR reacted with gold to form a red chelate of a molar ratio 1:3 (gold to HNAR). This chelate was enriched by the solid phase extraction with a polymer-based C_{18} cartridge and the retained chelate was eluted from the cartridge with dimethyl formamide (DMF). An enrichment factor of 100 was achieved. In DMF medium, the molar absorptivity of the chelate was found to be 1.51×10^5 L mol^{-1} cm^{-1} at 496 nm. Beer's law was obeyed in the range of 0.01~2 μg mL^{-1}. The relative standard deviation for eleven replicates with a concentration of 0.5 μg L^{-1} level was 2.31%. The detection limit based on three times the standard deviation was 0.01 μg L^{-1} in the original sample. This method was applied to the determination of gold with good results.

KEYWORDS

Gold, solid phase extraction, spectrophotometry, 5-(2-hydroxy-4-nitrophenylazo)-rhodanine.

1. Introduction

Gold is among those elements that have a very low natural abundance on earth. It is an important noble metal with relevance to the economy and has significant industrial applications. The development of a simple, sensitive and selective method for the determination of trace amounts of gold is therefore desirable. 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 atomic absorption spectrometry have been widely applied to the determination of gold.[1–9] The simplicity and low operating costs of spectrophotometric methods make them attractive as an alternative technique and a wide variety of spectrophotometric methods for the determination of gold have therefore been reported. Each of the reported chromogenic systems have their specific advantages and disadvantages with respect to sensitivity, selectivity and rapidity.[10–18] These standard spectrophotometric methods are, however, often not sensitive enough to determine gold ions in water or ore samples on the μg L^{-1} or ng L^{-1} levels. The determination of such low concentrations of gold usually requires a preconcentration step.

Solid phase extraction is an attractive technique because of it notable advantages.[19–23] In this paper, the colour reaction of 5-(2-hydroxy-4-nitrophenylazo)-rhodanine (HNAR) with gold and the solid phase extraction of Au-HNAR chelate with a reversed phase polymer-based C_{18} cartridge was studied. Based on this, a highly sensitive, selective and rapid method for the determination of gold in water and ore samples was developed.

2. Experimental

2.1. Apparatus

A UV-160 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, CA, USA). The extractions were carried out on a Waters Solid Phase Extraction (SPE) device (the device can carry out twenty extractions simultaneously) using a reversed phase C18™ polymer-based C_{18} cartridge (Beijing Genosys Technologies, P.R. China).

2.2. Synthesis of HNAR

HNAR was synthesized according to the following procedure: 1.54 g (0.01 mol) of 4-nitro-2-aminophenol was dissolved in 45 mL of 95% alcohol in a 100 mL beaker while stirring. To this solution 12.0 mL of 6.0 mol L^{-1} HCl was added and the solution was cooled to 0°C; 7.0 mL of a 10% $NaNO_2$ solution was then slowly added and the reaction was stirred for 15 min to give the respective diazonium salt. In another 200 mL beaker 1.48 g (1.11 mol) of rhodanine was dissolved in 14 mL of 7.5 mol L^{-1} aqueous ammonia and the solution was cooled to 0°C. The diazonium salt was then added dropwise to the rhodanine solution and the mixture was stirred overnight. Acidification of the obtained solution with concentrated HCl to pH 1 yielded a red precipitate. The precipitate was isolated by filtration. The crude product was re-crystallized three times with 90% ethanol to give pure HNAR in 68% yield. Its structure (Fig. 1) was be verified by IR, ^{1}H-NMR, MS spectrometry and elemental analysis. Elemental analysis: $C_9H_6N_4O_4S_2$, calculated (found),

---

* To whom correspondence should be addressed.
Tel: +86-871-5033895. E-mail: ygy1110@yahoo.com.cn

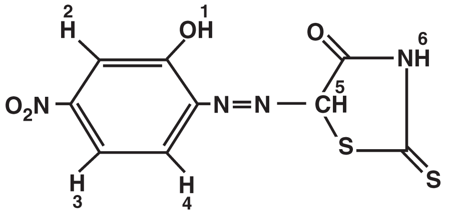

Figure 1 The structure of HNAR.

36.24 (35.95)% C, 2.03 (2.12)% H, 18.78 (18.96)% N, 21.50 (21.68)% S. IR (KBr) (cm^{-1}): 3600 (ν_{-OH}), 3275 (ν_{-N-H}); 3050, 3050 ($\nu_{=C-H}$); 1545, 1360($\nu_{-N=O}$); 1750 ($\delta_{C=O}$); 1645 (δ_{N-H}); 1540, 1505, 1440 ($\nu_{C=C}$); 1290 (ν_{C-N}); 1150, 1205 ($\nu_{C=S}$); 825 (δ_{Ar-H}); 805 ($\delta_{C=C-H}$). ^{1}H-NMR (solvent: acetone-d$_6$) (δ, ppm): 4.82 (1H, s, O-H, H 1); 7.65 (1 H, s, Ar-H, H 2); 7.74 (1 H, d, Ar-H, H 3); 7.22 (1 H, d, Ar-H, H 4); 2.58 (1H, s, -C-H, s, H 5). MS (EI) (m/z): 314 (M$^+$).

2.3. Reagents

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

2.4. General Procedure

To a standard or sample solution containing no more than 2.0 μg of Au(III) in a 100 mL calibrated flask were added 5 mL 5 mol L^{-1} phosphoric acid solution, 5.0 mL 3.0 × 10^{-4} mol L^{-1} HNAR solution and 3.0 mL 2.0% emulsifier-OP solution. The mixture was diluted to the mark and mixed well. After 10 min the solution was passed through a polymer-based C$_{18}$ cartridge at a flow rate of 20 mL min^{-1}. Following the completion of the enrichment step the retained chelate was eluted from the cartridge in reverse direction at a flow rate of 5 mL min^{-1} with 1.0 mL of DMF. The eluent was adjusted to exactly 1.0 mL in a 1.0 mL calibrated flask by adding microamounts of DMF with a 200 μl syringe. The absorbance of this solution was measured at 496 nm in a 1 cm microcell (0.5 mL) against a reagent blank prepared in a similar way without gold.

3. Results and Discussion

3.1. Absorption Spectra

Absorption spectra of HNAR and its Au(III) chelate are shown in Fig. 2. The absorption peaks of HNAR and its complex in DMF medium are located at 400 nm and 496 nm, respectively.

3.2. Effect of Acidity

Previous experiments had shown that the complexation of Au(III) with HNAR is best carried out in acidic medium. The effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid and acetic acid on the complex formation of Au(III) with HNAR was therefore studied. These experiments showed that phosphoric acid gave the best results and a concentration of phosphoric acid in a range of 0.05–0.5 mol L^{-1} was found to give the highest constant absorbance and the addition of 5 mL of phosphoric acid is therefore recommended.

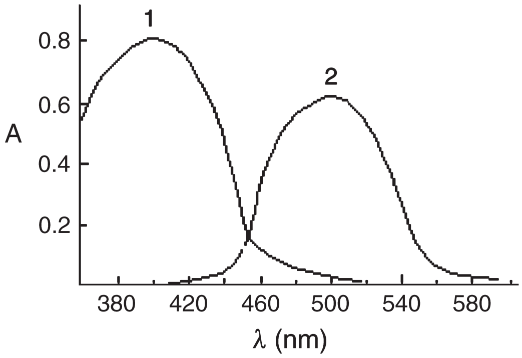

Figure 2 Absorption spectra of HNAR and its Au(III) complex: 1, HNAR-emulsifier-OP blank against water; 2, HNAR-emulsifier-OP-Au(III) chelate against reagent blank.

3.3. Effect of Surfactants

The effect of surfactants on the Au(III)-HNAR system was also studied. The experiments (Table 1) showed that the absence of surfactants or the presence of anionic or cationic surfactants led to a low intensity absorption, whereas the absorbance of the Au(III)-HNAR complex markedly increased in the presence of nonionic surfactants. The effect of nonionic surfactants on the absorbance followed the sequence: Emulsifier-OP > Tween-80 > Tween-20 > Tween-60. Further optimization of the chosen emulsifier-OP showed that the addition of 1.5~4 mL OP solution led to constant and high absorbance readings and the use of 3.0 mL is therefore recommended.

3.4. Effect of HNAR Concentration

The use of 5 mL of 3.0 × 10^{-4} mol L^{-1} of a HNAR solution was found to be sufficient for the complexation of up to 2.0 μg of Au(III). Accordingly, 5.0 mL of HNAR solution was added in all further measurement.

3.5. Stability of the Chromogenic System

After mixing the components, the absorbance reached its maximum within 5 min at room temperature and remained stable for at least 4 h. After having been extracted into DMF, the chelate was stable for at least 6 h.

3.6. Solid Phase Extraction

It was shown that HNAR forms stable chelate complexes with Au(III) in acidic medium. To meet the requirement of metal chelate enrichment by solid phase extraction in acidic medium, a reversed phase polymer-based C$_{18}$ cartridge was selected. Polymer-based C$_{18}$ is manufactured from a hydrophilic methacrylate polymer, which is functionalized with C$_{18}$ ligands and provides a broad range of solvent choices and a pH range

Table 1 The effect of surfactants on the Au(III)-HNAR chromogenic system.

Surfactant	No surfactant	Emulsifier-OP	Tween-80	Tween-20	Tween-60	SDS	CTMAB	CPB
λmax (nm)	488	496	492	486	486	480	480	480
ε (×10^4) L mol^{-1} cm^{-1}	9.18	15.1	13.6	12.2	11.8	8.92	8.18	8.26

Table 2 Tolerance limits for the determination of 0.5 μg of Au(III) with HNAR (relative error ±5%).

Ion added	Tolerance (mg)
NO_3^-, K^+, borate, Na^+	20
Li^+, Al^{3+}, PO_4^{3-}, NO_2^-, SO_4^{2-}, ClO_4^-	10
Ca^{2+}, Mg^{2+}, SO_3^{2-}, Sr^{2+}, Ba^{2+}, IO_3^-, BrO_3^-, ClO_3^-	5
Mn^{2+}, Ce(IV), W(VI), Mo(VI), U(IV), Fe^{3+}	2
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^+	0.05
Ir(IV) , Rh(III), Ru(III)	0.02
Pt(IV), Pd^{2+}, Hg^{2+}	0.01

from 0~14.

Both enrichment and elution were carried out on a Waters SPE device (the device can carry out twenty extractions simultaneously). The flow rate was set to 20 mL min^{-1} during enrichment and 5 mL min^{-1} during elution.

In experiments to investigate the retention of HNAR and its Au(III) chelate on the cartridge it was found that HNAR and its Au(III) chelate were quantitatively retained on the cartridge in phosphoric acid medium. The capacity of the cartridge was determined as 22 mg of Au(III)-HNAR chelate in 100 mL of solution. Since the maximum amount of gold in the present experiments was only 2.0 μg the cartridge has a more than adequate capacity to enrich the Au(III)-HNAR chelate.

In order to choose an appropriate eluant for the retained HNAR and its Au(III) chelate various organic solvents were studied. For the elution of the Au(III)-HNAR chelates from the cartridge the following solvent volumes were needed: 0.9 mL DMF, 1.1 mL isopentyl alcohol, 1.3 mL acetone, 1.4 mL acetonitrile, 1.6 mL ethanol and 1.8 mL methanol. The highest enrichment was achieved for DMF which was therefore selected as eluant. Reverse direction extraction was found to be more efficient than forward direction extraction. Based on these results DMF (1 mL) was chosen as eluant at a flow rate of 5 mL min^{-1}.

3.7. Calibration Curve and Sensitivity

The calibration curve showed that Beer's law is obeyed for 0.01~2.0 μg Au(III) per mL solution. The linear regression equation was determined to $A = 0.762\ C\ (\mu g\ mL^{-1}) + 0.0208$ ($r = 0.9994$). The molar absorptivity was calculated to be 1.51×10^5 L mol^{-1} cm^{-1} at 496 nm. The relative standard deviation at a concentration level of 0.5 μg L^{-1} of Au(III) (11 repeats) was 2.31%. The detection limit based on three times the standard deviation is 0.01 μg L^{-1}.

3.8. Interference

The selectivity of the proposed method is shown in Table 2 for the determination of 0.5 μg 100 mL^{-1} of Au(III) in the presence of various ions with a relative error of ±5%. It is evident that most common ions do not interfere with the determination, indicating the high selectivity of the method.

3.9. Composition of the Complex

The composition of the complex was determined as Au(III) to HNAR 1:3 by the method of continuous variations and the mole ratio method.

3.10. Application

Aqueous samples were acidified with phosphoric acid and filtered through a 0.45 μm filter and then analysed for gold according to the general procedure. The results (reagents blank is deducted) are shown in Table 3 together with results obtained from ICP-MS measurements for reference purposes. The recovery was tested by adding 0.4 μg of Au(III) per sample and the precision by carrying out five determinations of the same sample. Standard recovery and relative standard deviation are shown in Table 3.

The analysed ore samples were Chinese certified reference standard materials obtained from the Chinese Standard Material Center. The certified standard gold value is 0.410 g T^{-1} for GBW(E)070012 and 3.81 g T^{-1} for GBW(E)070014. For the determination, 2.0 g of ore was weighed into a 50 mL Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China) and 20 mL 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, 20 mL of 5% phosphoric acid was added and the mixture was heated close to the boiling point in order to leach the residue. The mixture was allowed to cool, filtered, and the insoluble residue was washed two times with 5% phosphoric acid. The combined solutions were collected in a 100 mL calibrated flask and analysed for gold according to the general procedure. The results (reagents blank is deducted) are shown in Table 3 together with reference values from an ICP-MS measurement. The recovery test by added 0.5 μg of Au(III) in sample and the precision test by five times determination of the same sample were also carried out. The results of the standard recovery and the relative standard deviation are shown in Table 3.

4. Conclusion

The proposed method has the following characteristics: (1) HNAR is a sensitive and selective spectrophotometric reagent for gold. The molar absorptivity of the chelate reaches 1.51×10^5 L mol^{-1} cm^{-1}. Most foreign ions do not interfere with the determination. (2) By solid phase extraction with C_{18} cartridge, the HNAR-Au(III) chelate in 100 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 100. The detection limit reaches 0.01 μg L^{-1} in the original samples, and μg L^{-1} level of gold can be determined with good results.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20471051) and the Key Natural Science Foundation of Yunnan Province (2005K021)

Table 3 Gold concentrations in the water and ore samples.

Samples	ICP-MS method	Found	RSD% (n = 5)	Recovery (%)
River water	11.2 (μg L^{-1})	13.1 (μg L^{-1})	3.5	91
Planting effluents	36.2 (μg L^{-1})	35.1 (μg L^{-1})	3.1	94
Ore GBW(E)070012	0.414 (g T^{-1})	0.406 (g T^{-1})	3.4	90
Ore GBW(E)070014	3.86 (g T^{-1})	3.74(g T^{-1})	2.6	95

References

1 T.S. Shigeru and T.C. Masahiro, *Bunseki. Kagaku.*, 1999, **48**, 847.
2 R.K. Malhotra, G.V. Ramanaiah and K. Satyanarayana, *At. Spectrosc.*, 1999, **20**, 92.
3 N. Zuzana and K. Petr, *Fresenius J. Anal.Chem.*, 2000, **367**, 369.
4 B. Lack, T. Nyokong and J. Duncan, *Anal. Chim. Acta.*, 1999, **385**, 393.
5 R.D. Ye and S.B. Khoo, *Analyst,* 1999, **124**, 353.
6 Q.F. Hu, G.Y. Yang, Z.J. Huang and J.Y. Yin, *Talanta,* 2002, **58**, 467.
7 M. Dequaire, C. Degrand and B. Limoges, *Anal. Chem.*, 2000, **72**, 5521.
8 O. Kiwamu, S. Gen and T. Yoshiyuki, *Chem. Geol.*, 1999, **157**, 189.
9 D.H. Gunther and A. Christoph, *J. Anal. At. Spectrom.*, 1999, **14**, 1363.
10 P. Anjali, *Talanta,* 1998, **46**, 583.
11 E. Tang, G.Y. Yang and J.Y. Yin, *Spectrochim, Acta. A.*, 2003, **59**, 651.
12 Z.T. Zeng and Q.H. Xu, *Talanta,* 1992, **39**, 409.
13 G.Y. Yang, Q.F. Hu, J.H. Yang, Z.J. Huang and J.Y. Yin, *Anal. Sci.*, 2003, **19**, 299.
14 F.M. EI-Zawawy, M.F. EI-Shahat, A.A. Mohamed and M.T.M. Zaki, *Analyst,* 1995, **120**, 549.
15 G.L. Long, J.D. Wineforder, *Anal. Chem.*, 1983, **55**, 712A.
16 G.L. Long and J.D. Wineforder, *Anal Chem.*, 1980, **52**, 2242.
17 J. Medinilla, F. Ales and F.G. Sanchez, *Talanta,* 1986, **33**, 329.
18 Z.J. Li, J.M. Pan and J. Tang, *Anal. Bioanal. Chem.*, 2003, **375**, 408.
19 Q.F. Hu, G.Y. Yang, J.Y. Yin, *J. Environ. Monit.*, 2002, **4**, 956.
20 Q.F. Hu, G.Y. Yang and J.Y. Yin, *Talanta,* 2002, **57**, 751.
21 Q.F. Hu, G.Y. Yang, Y.Y. Zhao and J.Y. Yin, *Anal. Bioanal. Chem.*, 2003, **375**, 831.
22 G.Y. Yang, X.C. Dong, Q.F. Hu and J.Y. Yin, *Anal. Lett.*, 2002, **35**, 1735.
23 Z. Li, G.Y. Yang, B.X. Wang, J.Y. Yin, *J. Chromatogr. A.*, 2002, **971**, 243.
24 Q.F. Hu, X.H. Wu, Z.J. Huang, G.Y. Yang and J.Y. Yin, *S. Afr. J. Chem.*, 2005, **58**, 64.