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Study on Solid Phase Extraction and Spectrophotometric Determination of Gold with 5-(2-Hydroxy-4-sulfo-5-chlorophenolazo)thiorhodmine as Chromogenic Reagent

JINGJING LIANG†, JISHOU ZHAO, YANQING YE, QIUFEN HU*† and GUANGYU YANG†
Department of Chemistry, Yunnan Nationalities University, Kunming 650031, P.R. China
E-mail: huqiufena@yahoo.com.cn

In this paper, a new method for the determination of gold based on the rapid reaction of gold with 5-(2-hydroxy-4-sulfo-5-chlorophenolazo) -thiorhodmine (HSCT) 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, HSCT reacts with gold to form a red chelate of a molar ratio 1:3 (gold to HSCT). This chelate was enriched by the solid phase extraction with a polymer-based C_{18} cartridge and eluted the retained chelate from the cartridge with dimethyl formamide. The enrichment factor of 100 was achieved. In the DMF medium, the molar absorptivity of the chelate is 1.32×10^5 L mol^{-1} cm^{-1} at 510 nm. Beer's law is obeyed in the range of 0.01-2.0 μg mL^{-1} in the measured solution. The relative standard deviation for eleven replicates sample of 0.5 μg L^{-1} level is 2.22 %. The detection limit, based on the three times of standard deviation is 0.03 μg L^{-1} in the original sample.

Key Words: 5-(2-Hydroxy-4-sulfo-5-chlorophenolazo)thiorhodmine, Gold, Solid phase extraction, Spectrophotometry.

INTRODUCTION

Gold is one of most important noble metals due to its wide application in industries, ornaments and economic activity. Therefore, simple, sensitive and selective method for determination of trace gold was strongly required[1,2]. Several sophisticated techniques, such as ICP-MS, ICP-AES, electrochemical, spectrofluorimetry and neutron activation analysis have widely been applied to the determination of gold[3]. Spectrophotometric method still has the advantages in respect of simplicity and low operating costs[4-10]. However, the routine spectrophotometric methods are often not sensitive enough to determine low concentration of gold ion. Consequently, a preconcentration step is usually required.

Solid phase extraction is an attractive technique because of it 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.

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†Department of Chemistry, Yuxi Teacher's College, Yuxi 653100, P.R. China.

However, the routine reserved phase silica-bond C_{18} cartridge only can use in pH range of 2-8. The chromogenic systems in acidic or alkaline medium not fit this cartridge. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, in this paper, the solid phase extraction of Au-HSCT (5-(2-hydroxy-4-sulfo-5-chlorophenolazo)thiorhodmine) chelate with a reversed phase polymer-based C_{18} cartridge was study. 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 provides a broad range of solvent choices and a pH range from 0-14. By using the polymer-based C_{18} cartridge, the Au-HSCT chelate was enriched by solid phase extraction in hydrochloric acid medium and the enrichment factor of 100 was achieved. Base on this, a highly sensitive, selective and rapid method for the determination of gold was developed.

EXPERIMENTAL

A UV-160 A spectrophotometer (Shimidzu 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 extraction was performed on Waters solid phase extraction (SPE) device (the device can prepare 20 samples simultaneously) and a reversed phase Polymer C_{18}™ polymer-based C_{18} cartridge (Beijing Genosys Technologies, P.R. China) was used.

All solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP reagent water system (Millipore Corporation, USA). HPLC grade dimethyl formamide (Fisher Corporation, USA) was used. 5-(2-Hydroxy-4-sulfo-5-chloro phenolazo)thiorhodmine (HSCT) was synthesized according to the literature[11] and a 3.0×10^{-4} mol L^{-1} of HSCT solution was prepared by dissolving HSCT in DMF. A stock standard solution of gold (1.0 mg mL^{-1}) was obtained from Chinese Material Standard Center, and a working solution of 0.5 μg mL^{-1} was prepared by diluting this solution. A 5 mol L^{-1} of hydrochloric acid was used. Emulsifier-OP solution (2.0 % (v/v)) was prepared by dissolving emulsifier-OP with water. All chemical used were of analytical grade unless otherwise stated.

Sample preparation: For clean water sample, the samples were acidified with hydrochloric acid, then filtrated by 0.45 μm filter and prepared for the following determination. (If there were organics in water interfere the determination, the sample was digested as following procedure: Taking an appropriate volume of sample in a 500 mL flask and concentrated the sample to about 20 mL by heating on a hot plate. To this solution, 5.0 mL of concentrated nitric acid, 2.0 mL of concentrated hydrochloric acid and 5 mL of 30 % hydrogen peroxide were added. The mixture was heated on hot plate till evaporated to near dryness. The residue was dissolved in 20 mL of 5 % of hydrochloric acid and prepared for the following determination.

General procedure: To a standard or sample solution containing not more than 2.0 mg of Au(III) in a 100 mL of calibrated flask, 5.0 mL of 5 mol L^{-1} of hydrochloric acid solution, 5.0 mL of 3.0×10^{-4} mol L^{-1} HSCT solution and 3.0 mL of 2.0 % emulsifier-OP 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 is eluted from the cartridge at a flow rate of 5.0 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 microamount of DMF with a 200 mL syringes. The absorbance of this solution was measured at 510 nm in a 1 cm microcells (0.5 mL) against a reagent blank prepared in a similar way without gold.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of HSCT and its Au(III) chelate were measured with spectrophotometer. The results (Fig. 1) show that the absorption peaks of HSCT and its Au(III) chelate in DMF medium are located at 400 nm and 510 nm, respectively.

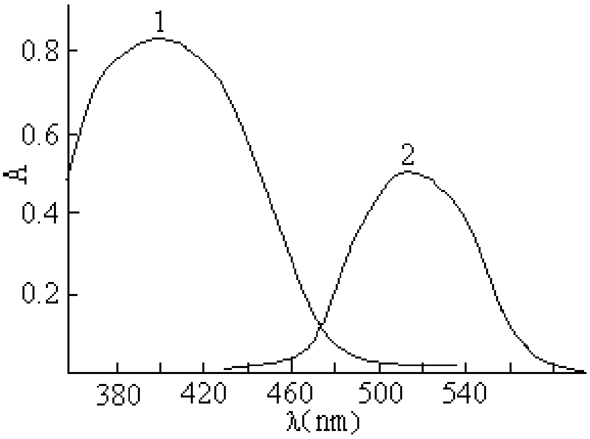

Fig. 1. Absorption spectra of HSCT and its Au(III) complex: 1, HSCT-emulsifier-OP blank against water; 2, HSCT-emulsifier-OP-Au(III) complex against reagent blank

Effect of acidity: The results showed that the optimal condition for the reaction of Au(III) with HSCT is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid and the like, on the colour reaction of Au(III) with HSCT was studied. The results 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 5.0 mol L^{-1} hydrochloric acid was recommended.

Effect of surfactants: The effects of surfactants on Au(III)-HSCT system were studied. The results show that in the absence of surfactants, anionic surfactants or cationic surfactants, the Au(III)-HSCT chromogenic system give a low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly. Several non-ionic 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 give a constant and maximum absorbance. Consequently, the use of 3.0 mL was recommended.

Effect of HSCT concentration: For up to 2.0 μg of Au(III), the use of 5 mL of 3.0×10^{-4} mol L^{-1} of HSCT solution was found to be sufficient for a complete reaction. Accordingly, 5.0 mL of HSCT solution were added in all further measurement.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 8.0 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: In this study, HSCT reacts with Au(III) and form stable chelates in acid medium. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, a reversed phase polymer-based C_{18} cartridge with pH range 0-14 was selected. 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 provides a broad range of solvent choices and a pH range from 0-14.

Both the enrichment and the elution were carried out on a Waters SPE device (the device can prepare 20 samples simultaneously). The flow rate was set to 20 mL min^{-1} when enrichment and 5 mL min^{-1} when elution. Some experiments were carried out in order to investigate the retention of HSCT and its Au(III) chelate on the cartridge. It was found that the HSCT 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 18 mg for Au(III)-HSCT chelate in a 100 mL of solution. In this experiment, the maximum amount of gold is only 2.0 μg. Therefore, the cartridge has adequate capacity to enrich the Au(III)-HSCT chelate. In order to choose a proper eluant for the retained HSCT and its Au(III) chelate, various organic solvents were studied. For eluting the Au(III)-HSCT 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, 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 HSCT and its Au(III) chelate in reverse direction than in forward direction, so it is necessary to upturned cartridge when elution. 1.0 mL of DMF was sufficient to elute the HSCT 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 0.01-2.0 mg Au(III) per mL in the measured solution. The linear regression equation obtained was A = 0.672 C (μg mL^{-1}) + 0.0115 (r = 0.9993). The molar absorptivity was calculated to be 1.32×10^5 L mol^{-1} cm^{-1} at 510 nm. The relative standard deviation at a concentration level of 0.5 μg L^{-1} of Au(III) (11 repeats determination) was 2.22 %. The detection limit, based on the three times of standard deviation is 0.03 mg L^{-1} in the original sample.

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

TABLE-1
TOLERANCE LIMITS FOR THE DETERMINATION OF 0.5 μg OF Au(III) WITH HSCT (RELATIVE ERROR ± 5 %)

Ion added	Tolerate (mg)
NO_3^-, K^+, borate, Na^+, PO_4^{3-}	20
Li^+, Al^{3+}, NO_2^-, SO_4^{2-}, ClO_4^-, Ca^{2+}, Mg^{2+}	10
SO_3^{2-}, Sr^{2+}, Ba^{2+}, IO_3^-, BrO_3^-, ClO_3^-, Fe^{2+}	5
Mn^{2+}, Ce^{4+}, W^{6+}, Mo^{6+}, U^{4+}, Fe^{3+}, Zn^{2+}	2
Ti^{4+}, Bi^{3+}), V^{5+}, Cr^{6+}, Zr^{4+}, F^-	1
Cd^{2+}, Cr^{3+}, La^{3+}, Sn^{4+}, Zr^{4+} , Co^{2+}, Ni^{2+}, Br^-	0.5
Ru^{3+}, Bi^{3+}, Pb^{2+}, Sb^{3+}, Th^{4+}, Os^{8+} , I^-, Cu^{2+}	0.2
Se^{4+}, Te^{4+}, $S_2O_3^{2-}$, Ag^+	0.1
Ir^{4+}, Rh^{3+}, Ru^{3+}	0.05
Pt^{4+}, Hg^{2+}	0.01
CN^-, SCN^-	0.005

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 HSCT is 1:3.

Application: This method was applied to the determination of gold in water samples. For the prepared samples, the gold contents were analyzed according to general procedure. An ICP-MS method[12] was used as a reference method and the result are shown in Table-2.

TABLE-2
DETERMINATION OF GOLD IN THE WATER SAMPLES

Samples	ICP-MS method (μg L^{-1})	Proposed method (μg L^{-1})	RSD % (n = 5)	Recovery (%) (n = 5)
River water	5.26	4.95	3.5	87
Effluent plants	22.8	24.6	3.3	92

Conclusion

In this method, 5-(2-hydroxy-4-sulfo-5-chlorophenolazo)thiorhodmine (HSCT) is a sensitive and selective spectrophotometric reagent for gold. The molar absorptivity of the chelate reaches 1.32 × 10^5 L mol^{-1} cm^{-1}. Most foreign ions do not interfere with the determination. The polymer-based C_{18} was used as solid phase extraction sorbent. By this sorbent, the Au-HSCT chelate was enriched in hydrochloric acid medium and the enrichment fact of 100 was achieved. The detection limit reaches 0.03 μg L^{-1} in the original samples and μg L^{-1} level of gold can be determined with good results.

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REFERENCES

1. H. Schmidbaur, S. Cronje and B. Djordjevic, *Chem. Phys.*, **311**, 151 (2005).
2. C. Milone, R. Ingoglia, G. Neri, A. Pistone and S. Galvagno, *App. Catal. A (Gen).*, **211**, 251 (2001).
3. R.R. Barefoot and J.C. Van Loon, *Talanta*, **49**, 1 (1999).
4. J. Karpinska, *Talanta*, **64**, 801 (2004).
5. Z.T. Zeng, T. Creedy and A. Townshend, *Anal. Chim. Acta*, **401**, 237 (1999).
6. P. Anjali, *Talanta*, **46**, 583 (1998).
7. L. Elci, S. Isildar and M. Dogan, *Anal. Chim. Acta*, **293**, 319 (1994).
8. Z.T. Zeng and Q.H. Xu, *Talanta*, **39**, 409 (1992).
9. E. Tang, G.Y. Yang and J.Y. Yin, *Spectrochim. Acta*, **59A**, 651 (2003).
10. Z.J. Li, J.M. Pan and J. Tang, *Anal. Bioanal. Chem.*, **375**, 408 (2003).
11. X.T. Tai, H.M. Bai, H.T. Li, Q.F. Hu, J.Y. Yin and G.Y. Yang, *Chin. J. Gold*, **25**, 42 (2004).
12. S.A. Dong, J. Chen and R.L. Wu, Analysis Methods of Precious Metals, Chinese Science Press, Beijing, P.R. China, edn. 1, pp. 263-268 (2004).

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