

Solid Phase Extraction and Spectrophotometric Method for Determination of Trace Gold with Octyl Benzimidazole Sulfide

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Synthesis and application of octyl benzimidazole sulfide (OBMS), as a new chromogenic reagent for the determination of gold has been described. Highly sensitive, selective and fast method for determination of gold based on its rapid reaction with OBMS and the solid phase extraction of the colored complex on a nonpolar resin MCI GEL CHP 20P has been developed. In the presence of 0.02-0.2 mol L⁻¹ of HCl solution and cetyl trimethylammonium bromide (CTMAB) medium, OBMS reacted with gold to form colored complex of gold-to-OBMS molar ratio of 1:2. The complex was enriched by the solid phase extraction with the MCI GEL CHP 20P cartridge. The complex was eluted from the cartridge with isopentyl alcohol and enrichment factor of 100 was achieved. In isopentyl alcohol medium, molar absorptivity of the complex was 2.77×10^5 L mol⁻¹ cm⁻¹ at 490 nm. Beer's law was obeyed in the concentration range 0.01 *ca.* 0.8 µg mL⁻¹. The relative standard deviation for 11 replicate samples at the 0.5 µg L⁻¹ level was 2.5 %. In the original sample detection limit was 0.04 µg L⁻¹. This method was applied to the determination of trace gold in ore samples with good result.

Key Words: Octyl benzimidazole sulfide, Gold, Solid phase extraction, Spectrophotometry.

INTRODUCTION

Gold is one of most important noble metals due to its wide application in industry and economic activity, yet it is not naturally abundant. Several sophisticated techniques, such as total reflection X-ray fluorescence spectrometry (TXRF), inductively coupled plasma mass spectrometry (ICP-MS), neutron activation analysis, inductively coupled plasma atomic emission spectrometry (ICP-AES), electrochemical, spectrofluorimetry, atomic absorption spectrometry, *etc.* have been widely applied to the determination of gold¹⁻¹². Some factors, including cost of instrumentation, technical know-how and costly maintenance of equipment restrict wider applicability of these techniques, particularly in the fieldwork and in laboratories with limited budgets in developing countries. Thus, development of a simple, sensitive and selective method for determination of trace amounts of gold is required.

Spectrophotometric methods are essentially applicable in trace analysis due to their simplicity and low operating costs. Usually they involve the use of chromogenic agents.

Spectrophotometry based determinations have been reported as useful alternatives to the other techniques for the analysis of gold. However, these can also suffer from interferences. There is a vast range of reagents which can be used, including 3,3',5,5'-tetramethylbenzidine hydrochloride¹³, methiomeprazine hydrochloride⁸, 2-aminoacetophenone isonicotinoyl hydrazone¹⁴, phenothiazine¹⁵, rhodanine derivatives¹⁶⁻¹⁸, 5-(4-sulphophenylazo)-8-aminoquinoline¹⁹, 2-mercaptobenzo-thiazole²⁰, etc. However, many of these lack sensitivity or selectivity. Standard spectrophotometric methods are, however, often not sensitive enough to determine gold ions in geological samples at $\mu\text{g L}^{-1}$ levels. Determination of such low concentrations of gold usually requires a pre-concentration step. For this purpose, one may utilize solid phase extraction due to its apparent advantages.

In this paper, the color reaction of octyl benzimidazole sulfide (OBMS) with gold and the solid phase extraction of Au(III)-OBMS complex on the MCI GEL CHP 20P cartridge has been described. Based on this, a highly sensitive, selective and rapid method for the determination of gold in ore samples has been developed.

EXPERIMENTAL

All reagents were of the highest available purity (at least of analytical grade). All the solutions were prepared with ultra-pure water obtained from a UPHW-1-90 reagent water system (Ulupure corporation, China). A $6.0 \times 10^{-3} \text{ mol L}^{-1}$ OBMS solution was prepared by dissolving OBMS with 95 % ethanol. A stock standard solution of gold (1.0 mg mL^{-1}) was obtained from the Chinese standard material center and a work solution of $0.2 \mu\text{g mL}^{-1}$ was prepared by diluting the stock standard solution. A 2.0 mol L^{-1} hydrochloric acid was used. Cetyl trimethylammonium bromide (CTMAB) solution (2.0 % w/v) was prepared by dissolving CTMAB with 20 % ethanol.

Synthesis of octyl benzimidazole sulfide (OBMS): Octyl benzimidazole sulfide was synthesized according to the following procedure: 2-mercaptobenzimidazole (7.50 g, 0.05 mol), acetone (100 mL) and KOH (3.36 g, 0.06 mol) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for *ca.* 0.5 h. 1-Bromooctane (11.59 g, 0.06 mol) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 5 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (30 mL), washed with water two times and dried with anhydrous Na_2SO_4 . The ether was evaporated and octyl benzimidazole sulfide was obtained. The precipitate was re-crystallized three times from 95 % ethanol to give a yield of 85 %. Melting point of the obtained product was 202-203 °C. Its structure (Fig. 1) was verified by elemental analysis, ^1H NMR, ^{13}C NMR and mass spectra. The results of elemental analysis are: $\text{C}_{15}\text{H}_{22}\text{N}_2\text{S}$, calculated (found), C 68.66 (68.78), H 8.46 (8.43), N 10.68(10.63); ^1H NMR (500 MHz, CDCl_3) δ 7.54 *ca.* 7.52 (m, 2H), 7.20 *ca.* 7.17 (m, 2H), 3.31 (t, $J = 7.4 \text{ Hz}$, 2H), 1.75 *ca.* 1.69 (m, 2H), 1.34 *ca.* 1.18 (m, 10H), 0.84 (t, $J = 6.9 \text{ Hz}$, 3H) ppm; ^{13}C NMR

(125 MHz, CDCl₃) δ 151.59, 139.82, 122.60, 114.46, 33.21, 32.17, 30.06, 29.53, 29.13, 23.02, 14.48 ppm; HRMS (ESI) *m/z*, calculated: 263.1576 (M+H)⁺; found: 263.1563 (M+H)⁺.

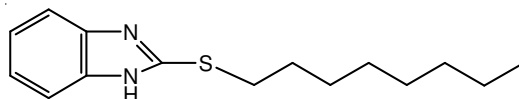


Fig. 1. Structure of octyl benzimidazole sulfide (OBMS)

A UV-1800 spectrophotometer (Shimadzu, Japan) equipped with 1 cm microcell (0.5 mL) was used for all absorbance measurements. pH was measured using a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

MCI GEL CHP 20P was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). MCI GEL CHP 20P resin is an aromatic type adsorbent (75-150 μm particle size). It is based on crosslinked polystyrenic matrix. MCI GEL CHP 20P is widely used in different industrial fields²¹. It was washed successively with methanol, water, 1.0 mol L⁻¹ HNO₃ in acetone, water, 1.0 mol L⁻¹ NaOH and water, sequentially.

General procedure: To either standard or sample solution containing *ca.* 0.8 μg of Au(III) in a 100 mL calibrated flask, 5 mL of 2.0 mol L⁻¹ HCl solution, 5 mL of 6.0 $\times 10^{-3}$ mol L⁻¹ OBMS solution and 6 mL 2.0 % CTMAB solution were added. The mixture was diluted to the mark and mixed well. After 5 min the solution was passed through the MCI GEL CHP 20P cartridge at the flow rate of 15 mL min⁻¹. After the enrichment step was completed, the retained complex was eluted from the cartridge with 1.0 mL of isopentyl alcohol at the flow rate of 1 mL min⁻¹ in reverse direction. The volume of the eluent was adjusted to 1.0 mL in a 1.0 mL calibrated flask by adding microamount of isopentyl alcohol with a 200 μL syringes. Absorbance of this solution was measured at 490 nm in a 1 cm microcell (0.5 mL) against the reagent blank prepared in a similar way without gold.

RESULTS AND DISCUSSION

Absorption spectra: Absorption spectra of OBMS and Au(III)-OBMS complex were recorded. Maximum absorbance of OBMS and Au(III)-OBMS complex were measured at 380 nm and 490 nm, respectively. The wavelength of 490 nm was chosen for further quantitative analysis (Fig. 2).

Effect of acidity: Previous experiments showed that the complex of Au(III) with OBMS proceeds the best in acidic medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid, acetic acid, *etc.*, on the color reaction of Au(III) with OBMS was studied. The highest and constant absorbance was obtained in the presence of hydrochloric acid in the concentration range: 0.02-0.2 mol L⁻¹. Thus, 5 mL of 2.0 mol L⁻¹ hydrochloric acid is recommended.

Effect of surfactants: Au(III)-OBMS complex was poorly soluble in aqueous solution. To enhance its solubility it is required to add a suitable amount of surfactants.

The experiments have shown that all type of surfactants: non-ionic, cationic, and anionic enhance solubility of the complex. Moreover, cationic surfactants improved sensitivity of determination of Au(III)-OBMS complex (Table-1).

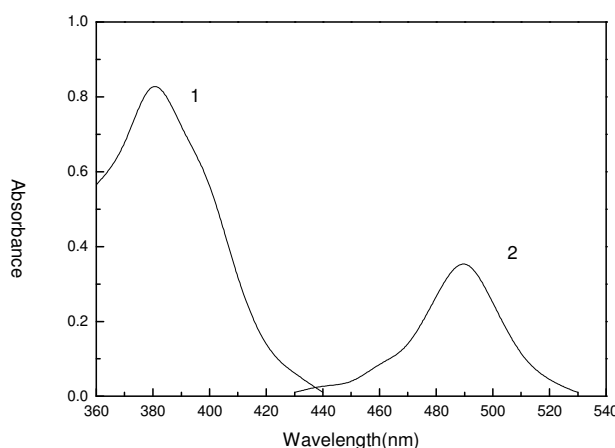


Fig. 2. Absorption spectra of OBMS and Au(III)-OBMS: **1.** OBMS-CTMAB blank against water; **2.** OBMS-CTMAB-Au(III) complex against reagent blank; The concentration of Au^{3+} is $1.52 \times 10^{-6} \text{ mol L}^{-1}$

TABLE-1
EFFECT OF SURFACTANTS ON THE Au(III)-OBMS CHROMOGENIC SYSTEM

	Absence	Emulsifier- OP	Tween- 80	Tween- 60	Tween- 20	CTMAB	CPB	SDS	SLS
λ_{max} (nm)	480	485	485	485	485	490	490	480	480
$\epsilon (\times 10^4)$ $\text{L mol}^{-1} \text{cm}^{-1}$	9.27	9.91	9.87	10.1	10.3	27.7	17.3	9.34	9.28

It appears from the data in Table-1 that cetyl trimethylammonium bromide (CTMAB) is the most appropriate surfactant and 0.08-0.20 % of CTMAB solution provided constant and maximum absorbance in present studies. Accordingly, 6 mL 2 % of CTMAB solution was added in further measurements.

Effect of OBMS concentration: For up to 0.8 μg of Au(III), the use of about 3-7 mL of $6.0 \times 10^{-3} \text{ mol L}^{-1}$ OBMS solution was found to be sufficient for complete reaction. Accordingly, 5 mL OBMS solution was added in all further measurement.

Solid phase extraction: It has been shown that OBMS forms stable complex with Au(III) in hydrochloric acid medium. To meet the requirement of metal complex enrichment by solid phase extraction in hydrochloric acid medium, the MCI GEL CHP 20P cartridge was used. Both enrichment and elution were carried out on an UCT SPE device. The flow rate was set to 15 mL min^{-1} during enrichment and to 1 mL min^{-1} during elution. It has been found experimentally that OBMS and its Au(III) complex are quantitatively retained on the cartridge in hydrochloric acid medium.

0.1 g of the MCI GEL CHP 20P sorbent was placed in the conical flasks (one cartridge of the MCI GEL CHP 20P contained 1 g of the sorbent). Stock solution of Au(III), CTMAB, hydrochloric acid and OBMS were added to the flask. The solutions were mixed thoroughly in a mechanical shaker. Concentration of Au(III) was measured by ICP-MS as soon as the equilibrium was reached. The maximum adsorption capacity of the MCI GEL CHP 20P cartridge was 3.05×10^{-4} mol g⁻¹ for Au(III).

Since the maximum amount of Au(III) in the performed experiments was only 4.06×10^{-9} mol, the cartridge (1 g) had more than enough capacity to enrich the Au(III)-OBMS complex.

In order to choose an appropriate eluent for the retained Au(III)-OBMS complex, after extraction of 4.06×10^{-9} mol of gold from the solution, gold ions were eluted with different eluting agents, such as ethanol, methanol, acetonitrile, isopentyl alcohol, acetone. Their elution efficiency decreased in the following sequence: isopentyl alcohol > ethanol > methanol > acetonitrile > acetone. Finally, isopentyl alcohol was selected as the appropriate eluent. Quantitative recovery (> 98 %) was obtained using 1.0 mL of isopentyl alcohol at the flow rate of 1 mL min⁻¹. In the subsequent experiments, 1.0 mL of isopentyl alcohol was used as the eluent to desorb the Au(III)-OBMS complex.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 5 min at room temperature and remains stable for 6 h in aqueous solution. After having been extracted into isopentyl alcohol, the complex was stable for at least 8 h.

Calibration curve and sensitivity: The calibration curve show that Beer's law is obeyed in the concentration range of 0.01-0.8 µg Au(III) per mL in the measured solution. The linear regression equation obtained was: $A = 1.42 C (\mu\text{g mL}^{-1}) - 0.0121$ ($r = 0.9992$). The molar absorptivity was calculated to be 2.77×10^5 L mol⁻¹ cm⁻¹ at 490 nm. The detection limit, based on 3 times the relative standard deviation of the blank, was 0.04 µg L⁻¹ in the original sample.

The relative standard deviation at the concentration level of 0.5 µg L⁻¹ of Au(III) (11 repeats) was 2.5 %.

Composition of the complex: The composition of the complex was determined by the continuous variation and the molar ratio method. Both showed that the molar ratio of Au(III) to OBMS is 1:2.

Interference: The selectivity of the proposed method is shown in Table-2 for the determination of 0.3 µg/100 mL 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. This method has high selectivity.

Applied to the catalyst sample: The developed method has been successfully applied to the determination of gold in ore samples (Table-3).

The 1.0000 g of ore sample was transferred into a porcelain crucible and roasted for 2.5 h in a muffle furnace at 600 °C. After roasting, the samples were transferred to 200 mL beaker and 50 mL freshly prepared aqua regia was added to sample. 0.5 g

TABLE-2
TOLERANCE LIMITS FOR THE DETERMINATION OF 0.3 µg of Au(III) WITH OBMS
(RELATIVE ERROR ± 5 %)

Ion added	Tolerate, (mg)
ClO ₃ ⁻ , K ⁺ , SO ₄ ²⁻ , Ca ²⁺	16
F ⁻ , Co ²⁺ , NO ₃ ⁻ , Cu ²⁺ , Zn ²⁺	10
IO ₃ ⁻ , Na ⁺ , I ⁻ , Br ⁻	5
Al ³⁺ , S ₂ O ₃ ²⁻ , SO ₃ ²⁻	3
Mg ²⁺ , Ba ²⁺ , BrO ₃ ⁻	2
Ni ²⁺ , Fe ²⁺ , Rh ³⁺ , Ir ³⁺	1
Pt ⁴⁺	0.8
Ag ⁺ , Fe ³⁺	0.4
Pd ²⁺	0.03

TABLE-3
DETERMINATION OF GOLD IN THE ORE SAMPLES (n = 5)

Samples	ICP-MS method (µg g ⁻¹)	Found (µg g ⁻¹)	RSD (%) (n = 5)	Recovery (%) (n = 5)
GBW(E)070022	2.36	2.31	3.1	95
GBW(E)070023	3.60	3.66	2.9	94
GBW07230	1.33	1.29	2.7	97

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 4 h and more aqua regia was added at regular intervals to maintain the free acid level at about one centimeter above the sample level. The watch glasses were then removed and the content was evaporated slowly until the residue became nearly dry. Then 30 mL of 6 mol L⁻¹ HCl was added to the beaker and the mixture was heated to dryness. This last step was repeated twice to ensure total elimination of HNO₃. The residue was diluted with 0.1 mol L⁻¹ 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⁻¹ HCl. The filtrate was collected into a 100 mL of calibrated flask quantitatively and the gold contents were analyzed according to the general procedure.

Conclusion

Proposed method has the following characteristics: (i) Octyl benzimidazole sulfide (OBMS) is a sensitive and selective spectrophotometric reagent for determination gold. Molar absorptivity of the complex reaches 2.77×10^5 L mol⁻¹ cm⁻¹. Most foreign ions do not interfere during determination. This is advantageous if traces of gold in ore samples are to be determined directly. (ii) Au(III)-OBMS complex in 100 mL solution can be concentrated up to 1.0 mL representing enrichment factor of 100, when solid phase extraction on MCI GEL CHP 20P cartridge is applied. Detection limit reaches 0.04 µg L⁻¹ in original samples and gold can be

determined at a $\mu\text{g L}^{-1}$ level with gold results. Octyl benzimidazole sulfide is cheap and can be easily synthesized. Its synthesis requires short reaction time and simple conditions and proceeds with a high yield. Therefore, proposed method can be applied to routine analysis.

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