# Solid phase extraction and a spectrophotometric method for the determination of trace amounts of gold with 4-rhodanineazo benzoic acid

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*Abstract*: The synthesis and application of 4-rhodanineazo benzoic acid (4--BARA) as a new chromogenic reagent for the determination of gold is described. A highly sensitive, selective, and fast method for the determination of gold based on its rapid reaction with 4-rhodanineazo benzoic acid and the solid phase extraction of the colored complex on a reversed phase Clean-up® C$_5$ cartridge was developed. In the presence of 0.02–0.2 mol/L phosphoric acid solution and a polyoxyethylene nonylphenol ether (emulsifier-OP) medium, 4-rhodanineazo benzoic acid reacted with gold to form a colored complex with a gold-to-4-BARA molar ratio of 1:2. The complex was enriched by solid phase extraction with a reversed phase Clean-up® C$_5$ cartridge. The complex was eluted from the cartridge with ethanol and an enrichment factor of 50 was achieved. In ethanol medium, the molar absorptivity of the complex was $2.39\times10^5$ L mol$^{-1}$ cm$^{-1}$ at 505 nm. The Beer Law was obeyed in the concentration range 0.01–~1.2 µg/mL. The relative standard deviation for eleven replicate samples at the 0.001 µg/mL level was 2.3 %. In the original sample, the detection limit was $8.0\times10^{-5}$ µg/mL. This method was applied to the determination of trace amounts of gold in ore samples with good result.

*Keywords*: 4-rhodanineazo benzoic acid; gold; spectrophotometry; solid phase extraction.

## INTRODUCTION

Gold is one of most important noble metals due to its wide application in industry and economic value, 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 optical emission spectrometry (ICP–OES), electrochemical, spectrofluorimetry, atomic absorption spectrometry, *etc*, have been

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widely applied to the determination of gold.[1–12] Some factors , including the cost of the instrumentation, technical know-how, and costly maintenance of equipment restrict wider applicability of these techniques, particularly in fieldwork and in laboratories in developing countries with limited budgets. Thus, the 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. The already reported chromogenic systems for the determination of gold have specific advantages and disadvantages with respect to sensitivity, selectivity and rapidity.[13–18] Standard spectrophotometric methods are, however, often not sensitive enough to determine gold ions in geological samples at the µg/L levels. Determination of such low concentrations of gold usually requires a pre-concentration step. For this purpose, solid phase extraction may be utilized due to its apparent advantages.

In this paper, the solid phase extraction of the Au(III)–4-BARA complex on a reversed phase Clean-up® $C_5$ cartridge is described. Based on this, a highly sensitive, selective and rapid method for the determination of gold in ore samples was developed.

## EXPERIMENTAL

*Apparatus*

A UV-1800 spectrophotometer (Shimadzu, Japan) equipped with 1 cm microcell (0.5 mL) was used for all absorbance measurements. The pH was measured using a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China). The extractions were realized on an UCT solid phase extraction device capable of performing 20 extractions simultaneously and using a reversed phase Clean-up® $C_5$ cartridge (Unitie Chemical Technologies Corporation, United States).

*Synthesis of 4-BARA*

4-BARA was synthesized according to a previously proposed procedure:[19] 1.37 g (0.0100 mol) of 4-aminobenzoic acid was dissolved in 25 mL of 95 % ethanol in a 100 mL beaker under stirring. To this solution, 10.0 mL of 6.0 mol/L HCl was added and the solution was cooled to 0 °C, 7.0 mL of a 10 % sodium nitrite solution was then slowly added and the reaction was stirred for 15 min to give the respective diazonium salt. In another 200 mL beaker, 1.33 g (0.01 mol) of rhodanine was dissolved in 14 mL of 7.5 mol/L 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. The precipitate was isolated by filtration. The crude product was re-crystallized three times with 95 % ethanol to give pure 4-BARA in 75 % yield; its melting point was 258 °C.

*Reagents*

All employed reagents were of the highest available purity (at least of analytical grade). All solutions were prepared with ultra-pure water obtained from a UPHW-1-90 reagent water system (Ulupure Corporation, China). A $6.0\times10^{-3}$ mol/L 4-BARA solution was prepared by

dissolving 4-BARA in 95 % ethanol. A stock standard solution of gold (1000 µg/mL) was obtained from the Chinese Standard Material Center, and a working solution of 0.20 µg/mL was prepared by diluting the stock standard solution. A 1.0 mol/L phosphoric acid was used. Polyoxyethylene nonylphenol ether (emulsifier-OP) solution (2.0 % w/v) was prepared by dissolving 2.0 g of emulsifier-OP in 100 mL of water.

*General procedure*

To either a standard or a sample solution containing no more than 1.2 µg of Au(III) in a 50 mL volumetric flask, 4.0 mL of a 1.0 mol/L phosphoric acid solution, 4.0 mL of a $6.0\times10^{-3}$ mol/L 4-BARA solution and 3.0 mL of a 2.0 % emulsifier-OP solution were added. The mixture was diluted to the mark and mixed well. After 6 min, the solution was passed through a Clean-up® $C_5$ cartridge at a flow rate of 10 mL/min. After completion of the enrichment step, the retained complex was eluted from the cartridge with 1.0 mL of ethanol at a flow rate of 1.0 mL/min in the reverse direction. The volume of the eluent was adjusted to 1.0 mL in a 1.0 mL volumetric flask by adding a microamount of ethanol with a 200 µL syringe. The absorbance of this solution was measured at 505 nm in a 1.0 cm microcell (0.50 mL) against a reagent blank prepared in a similar way but without gold.

*Determination of gold in ores*

An ore sample (1.0000 g) was transferred into a porcelain crucible and roasted for 2 h in a muffle furnace at 650 °C. After roasting, the sample was transferred to a 250 mL beaker and 50 mL freshly prepared *aqua regia* was added to the sample. NaCl (0.50 g) 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 1 cm above the sample level. The watch glass was then removed and the content was evaporated slowly until the residue became nearly dry. Then 40 mL of 6.0 mol/L HCl was added to the beaker and the solution was warmed until it became clear. Subsequently, the sample solution was cooled and filtered through an 11 µm Whatman No. 1 filter paper. The residue was washed with the minimum amount of 0.10 mol/L HCl. The filtrate was quantitatively collected into a 100 mL volumetric flask and the gold content was analyzed according to the general procedure.

## RESULTS AND DISCUSSION

*Absorption spectra*

The absorption spectra of 4-BARA and the Au(III)–4-BARA complex were recorded. The maximum absorbance of 4-BARA and the Au(III)–4-BARA complex were registered at 415 and 505 nm, respectively. The wavelength of 505 nm was chosen for further quantitative analysis (Fig. 1).

*Effect of acidity*

The pH of the solution is one of the important factors affecting the formation of complexes; the highest signal intensity of Au was obtained 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 4-BARA was studied. The results (Fig. 2) showed that phosphoric acid had the best effect and a

concentration of phosphoric acid within the 0.02–0.2 mol/L range was found to give the maximum and constant absorbance. Thus, 4.0 mL of 1.0 mol/L phosphoric acid is recommended.
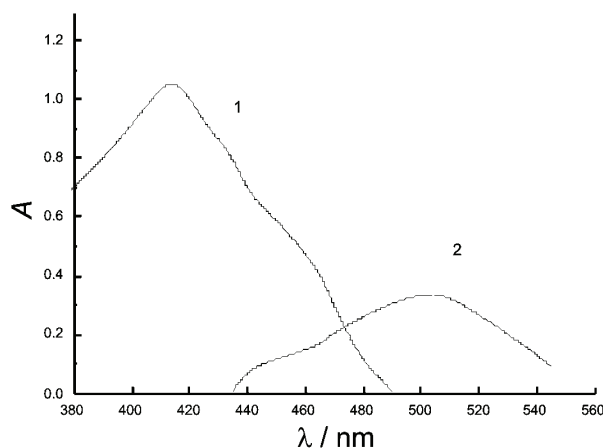


Fig. 1. Absorption spectra of 4-BARA and Au(III)–4-BARA: 1) 4-BARA-emulsifier-OP blank against water; 2) 4-BARA-emulsifier-OP–Au(III) chelate against reagent blank. The concentration of Au(III) was 0.30 μg/mL.
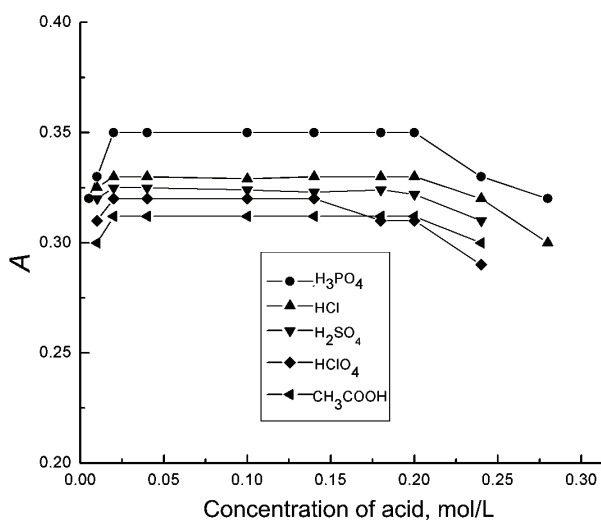


Fig. 2. The effect of acidity on the color reaction of Au(III) with 4-BARA. The absorbance was measured at 505 nm against the corresponding reagent blank. The concentration of Au(III) was 0.30 μg/mL. The other conditions were as given in the general procedure.

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*Effect of surfactants*

The Au(III)–4-BARA complex was poorly soluble in aqueous solution. To enhance its solubility, a suitable amount of surfactant had to be added. The experiments showed that all types of surfactants: nonionic (Emulsifier-OP, Tween-20, Tween-60, and Tween-80), cationic (CTAB, CPC) and anionic (SDS and SLES) enhanced the solubility of the complex. Moreover, the nonionic surfactants improved the sensitivity of the determination of the Au(III)-4- BARA complex (Table I).

TABLE I. The effect of the surfactants on the Au(III)–4-BARA chromogenic system

| Quantity | Absence | Emulsifier-OP | Tween- | | | CTAB | CPC | SDS | SLES |
|---|---|---|---|---|---|---|---|---|---|
| | | | 80 | 60 | 20 | | | | |
| $\lambda_{max}$ / nm | 490 | 500 | 500 | 500 | 500 | 490 | 490 | 490 | 490 |
| $\varepsilon$ / $10^{-4}$ L mol$^{-1}$ cm$^{-1}$ | 5.97 | 23.9 | 14.3 | 12.8 | 10.9 | 7.68 | 7.12 | 6.54 | 6.38 |

The molecule of sodium dodecyl sulfate (SDS) has a tail of 12 carbon atoms attached to a sulfate group, giving the molecule amphiphilic properties. Sodium laureth sulfates (SLES) are characterized by the alkyl chain length, the average ethylene oxide (EO) level and the EO distribution. The critical micelle concentration (CMC) value of cetriamonium bromide (CTAB) is 0.987 mM in pure water at 298 K. Cetylpyridinium chloride (CPC) is a cationic quaternary ammonium compound containing a pyridinium group and a 16 carbon hydrophobic tail. Polysorbate 20 (Tween-20), polysorbate 60 (Tween-60) and polysorbate 80 (Tween--80) are polysorbate surfactants. The number following the polysorbate part is related to the type of fatty acid associated with the polyoxyethylene sorbitan part of the molecule. Monolaurate is indicated by 20, monostearate by 60 and mono-oleate by 80.

From the data in Table I, it can be seen that polyoxyethylene nonylphenol ether (emulsifier-OP) is the most appropriate surfactant. Emulsifier-OP is a nonionic surfactant, the molecule of which contains both a hydrophobic tail (nonylphenol part) and a hydrophilic polar head group (ethoxy chain part), which imparts solubility in both aqueous and oil phases and reduces the surface tension of liquids. Emulsifier-OP does not dissociate in aqueous solutions, unlike anionic surfactants with negatively charged molecules and cationic surfactants of positively charged molecules in aqueous solution. Emulsifier-OP is non-ionic in solutions; hence its molecules have no electric charge. Thus, it can be successively employed in hard water at low temperatures and is stable in acidic and alkaline solutions. Emulsifier-OP shows excellent solvency and chemical stability, and is more widely used as a solubilizer than ionic surfactants. A 0.080–0.20 % solution of emulsifier-OP solution provided constant and maximum absorbance in the pre-

sent studies. Accordingly, 3.0 mL of a 2.0 % solution of emulsifier-OP was added in the further measurements.

*Effect of 4-BARA concentration*

For up to 1.2 µg of Au(III), the use of about 2–6 mL of a $6.0 \times 10^{-3}$ mol/L 4-BARA solution (Fig. 3) was found to be sufficient for complete reaction. Accordingly, 4.0 mL 4-BARA solution was added in all further measurements.
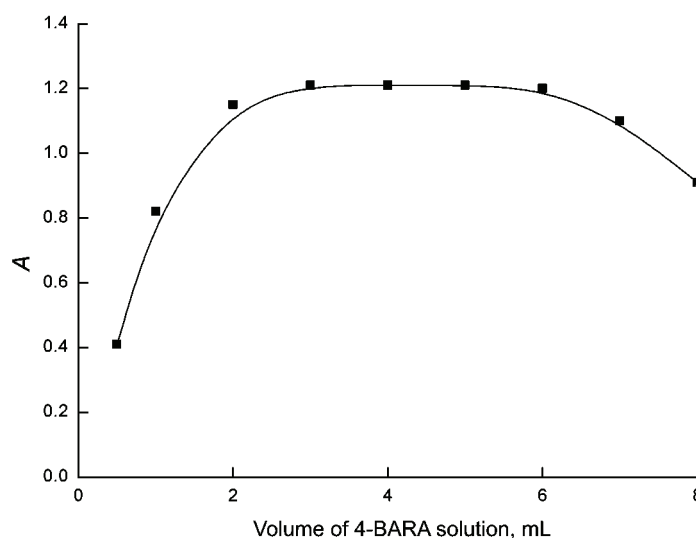


Fig. 3. The effect of the 4-BARA concentration on the color reaction of Au(III) with 4-BARA. The absorbance was measured at 505 nm against the corresponding reagent blank. The concentration of Au(III) was 1.0 µg/mL. The other conditions were as given in the general procedure.

*Solid phase extraction*

It was shown that 4-BARA forms a stable complex with Au(III) in phosphoric acid medium. To meet the requirement of metal complex enrichment by solid phase extraction in phosphoric acid medium, a Clean-up® $C_5$ cartridge was used. Both enrichment and elution were performed on a UCT SPE device. The flow rate was set to 10 mL/min during the enrichment and to 1 mL/min during elution. It was found experimentally that 4-BARA and its Au(III) complex are quantitatively retained on the cartridge in phosphoric acid medium.

0.10 g of Clean-up® $C_5$, $C_8$, $C_{10}$, $C_{12}$ and $C_{18}$ sorbents were placed in conical flasks (one cartridge of the Clean-up® contained 1.0 g of the sorbent). Stock solutions of Au(III), emulsifier-OP, phosphoric acid and 4-BARA were added to the flask. The solutions were thoroughly mixed using a mechanical shaker. The concentration of Au(III) was measured by ICP–MS as soon as the equilibrium

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was attained. The adsorption capacities of the Clean-up® cartridges for Au(III) were measured and are given in Table II.

TABLE II. The absorption capacity of different Clean-up® cartridges for Au(III)

| Clean-up® cartridges | $C_5$ | $C_8$ | $C_{10}$ | $C_{12}$ | $C_{18}$ |
|---|---|---|---|---|---|
| Adsorption capacity, mmol/g | 0.254 | 0.203 | 0.178 | 0.127 | 0.107 |

The Clean-up® $C_5$ cartridge was found to have the maximum adsorption capacity for Au(III). It appears that Clean-up® $C_5$ is the most appropriate sorbent for the considered purpose.

Since the maximum amount of Au(III) in the performed experiments was only $6.1\times10^{-9}$ mol, the cartridge (1.0 g) had more than enough capacity to enrich the Au(III)–4-BARA complex.

In order to choose an appropriate eluent for the retained Au(III)–4-BARA complex, after extraction of $6.1\times10^{-9}$ mol of gold from the solution, the gold ions were eluted with different eluting agents, *i.e.*, ethanol, methanol, acetonitrile, isopentylol and acetone. Their elution efficiency decreased in the following sequence: ethanol > isopentylol > methanol > acetonitrile > acetone. Finally, ethanol was selected as the appropriate eluent. Quantitative recovery (>98 %) was obtained using 1.0 mL of ethanol at a flow rate of 1.0 mL/min. In the subsequent experiments, 1.0 mL of ethanol was used as the eluent to desorb the Au(III)–4-BARA complex from the cartridge.

*Stability of the chromogenic system*

After mixing the components, the absorbance attained its maximum within 6 min at room temperature and remained stable for 5 h in aqueous solution. After extraction into ethanol, the complex was stable for at least 9 h.

*Calibration curve and sensitivity*

The calibration curve showed that the Beer Law was obeyed in the concentration range ~0.01 to ~1.2 µg Au(III) per mL in the measured solution. The obtained linear regression equation was: $A = 1.23c$ (µg/mL) – 0.0142 ($r = 0.9991$). The molar absorptivity was calculated to be $2.39\times10^5$ L mol$^{-1}$ cm$^{-1}$ at 505 nm. The detection limit, based on 3 times the relative standard deviation of the blank, was $8.0\times10^{-5}$ µg/mL in the original sample.

The relative standard deviation at the concentration level 0.001 µg/mL of Au(III) (11 repeats) was 2.3 %. The quantification limit (*LOQ*) of developed methods was $2.0\times10^{-4}$ µg/mL.

*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 4-BARA was 1:2.

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*Interference*

The selectivity of the proposed method is shown in Table III for the determination of 12 µg/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 a high selectivity.

TABLE III. Tolerance limits for the determination of 0.60 µg of Au(III) with 4-BARA (relative error ±5 %)

| Ion added | Tolerance, mg |
|---|---|
| $NO_2^-$, $F^-$, $Cl^-$, $K^+$, $SO_4^{2-}$, $Ca^{2+}$ | 60 |
| $Fe^{3+}$, $Pb^{2+}$, $NO_3^-$, $Cu^{2+}$, $Zn^{2+}$ | 30 |
| $Na^+$, $SO_3^{2-}$, $ClO_3^-$, $Ni^{2+}$, $I^-$ | 10 |
| $Al^{3+}$, $S_2O_3^{2-}$, $ClO_4^-$ | 5 |
| $Mg^{2+}$, $Ba^{2+}$, $Cd^{2+}$, $IO_3^-$, $BrO_3^-$ | 3 |
| $Mn^{2+}$, $Li^+$, Ce(IV), W(VI), Mo(VI), $Co^{2+}$ | 2 |
| Ti(IV), Bi(III), Cr(VI), Zr(IV), $Fe^{2+}$ | 1 |
| $Cr^{3+}$, $La^{3+}$, $Ag^+$, Sn(IV), U(IV), V(V), Th(IV) | 0.5 |
| $Sr^{2+}$, $Sb^{3+}$, $Br^-$, Os(VIII) | 0.2 |
| Se(IV), Rh(III), Te(IV), $Hg^{2+}$ | 0.1 |
| Ir(IV), Ru(III) | 0.05 |
| $Pd^{2+}$ | 0.04 |

*Application to real samples*

The developed method was successfully applied to the determination of gold in ore samples (Table IV).

TABLE IV. Determination of gold in ore samples ($n = 5$)

| Samples | ICP–MS method µg/g | Found µg/g | *RSD* % | Recovery % |
|---|---|---|---|---|
| GBW(E)070021 | 1.38 | 1.42 | 3.1 | 95 |
| GBW(E)070022 | 1.53 | 1.56 | 2.7 | 97 |
| GBW(E)070023 | 2.12 | 2.07 | 2.9 | 94 |

CONCLUSIONS

The proposed method has the following characteristics: 1) 4-BARA is a sensitive and selective spectrophotometric reagent for the determination gold. The molar absorptivity of the Au(III)–4-BARA complex is $2.39 \times 10^5$ L mol$^{-1}$ cm$^{-1}$. Most foreign ions do not interfere during the determination. The method is especially selective with respect to noble metal elements, which commonly interfere seriously in the determination of gold performed by literature methods. This is advantageous if traces of gold in ore samples are to be determined directly and 2) the Au(III)–4-BARA complex in 50 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 50, when solid phase extraction on a Clean-

-up® C$_5$ cartridge is applied. The detection limit is $8.0\times10^{-5}$ µg/mL in original sample and gold can be determined at the µg/L level with good results. 4-Rhodanineazo benzoic acid (4-BARA) is cheap and can be easily synthesized. Its synthesis requires a short reaction time and simple conditions and proceeds with a high yield. Therefore, the proposed method can be applied in routine analysis.

ИЗВОД

ЕКСТРАКЦИЈА ЧВРСОМ ФАЗОМ И СПЕКТРОФОТОМЕТРИЈСКА МЕТОДА ЗА ОДРЕЂИВАЊЕ ТРАГОВА ЗЛАТА СА 4-РОДАНИНАЗОБЕНЗОЕВОМ КИСЕЛИНОМ

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У раду је описана синтеза и примена 4-родениназо-бензоеве (4-БАРА) киселине као новог хромогеног реагенса. Високо осетљива, селективна и брза метода за одређивање злата базирана је на реакцији са 4-БАРА и екстракцији обојеног комплекса на Clean-up® C$_5$ колони реверсних фаза. У присуству 0,02–0,2 mol/L раствора фосфорне киселине и полиокси-етиленнонилфенил етра (emulsifier-OP) 4-БАРА формира са златом комплекс у стехиометријском односу 2:1. После сорпције на колони комплекс се елуира етанолом, са фактором концентрисања 50. У етанолу, коефицијент моларне апсорпције комплекса износи $2,39\times10^5$ L mol$^{-1}$ cm$^{-1}$ на 505 nm. Зависнос апсорбанције од концентрације следи Beer-ов закон у опсегу ~0,01–~1,2 µg/mL. Релативна стандардна девијација на концентрационом нивоу од 0,001 µg/mL износи 2,3 %, а границе детекције у оргиналном узорку $8,0\times10^{-5}$ µg/mL. Метода је успешно примењена за одређивање злата у узорцима руда.

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