

## Study on Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Trace Gold

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A new method was developed for the separation and preconcentration of Au(III) ions based on its complex formation with 2-carboxyl-1-naphthalthiorhodanine (CNTR) loaded on graphitized carbon black as a sorbent in a cartridge. The preconcentrated ions were eluted from the cartridge by passing 2.0 mL 0.1 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution through the solid support and then the Au(III) contents was measured by flame atomic absorption spectrometry. Conditions for preparation of the graphitized carbon black loaded with CNTR, pH and flow rate variables were studied, as well as, the effect of potential interfering ions. A preconcentration factor of 500 was achieved under the optimum conditions. The detection limit of the method was 0.05 µg L<sup>-1</sup> for Au(III). The method was successfully applied to the determination of Au(III) in water and ore samples. The relative standard deviations were below 3.3 % with recoveries of 88-104 %. The determination results were agreed with that of reference method (ICP-MS method).

**Key Words:** Gold, Graphitized carbon black, 2-Carboxyl-1-naphthalthiorhodanine, Solid phase extraction, FAAS.

### INTRODUCTION

Gold belongs to the elements which occur on the earth with very low natural contents. It is one of most important noble metals due to its wide application in industry and in economic activity. For this reason, a simple, sensitive and selective method for determination of trace gold was required<sup>1,2</sup>. Flame atomic absorption (FAAS) and emission spectrometry are the most widely used methods for trace gold determination<sup>3-5</sup>. However, because of the limited sensitivity of the FAAS, complex matrices and the low gold concentration levels in natural samples, the gold determination frequently requires a previous separation and preconcentration steps. The most widely used preconcentration methods are coprecipitation, ion exchange, solvent extraction, flotation and solid phase extraction (SPE)<sup>6-10</sup>.

Solid phase extraction is an attractive separation-preconcentration technique because of its some important advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents and environment friendly). Various solid phase extraction materials

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have been successfully used for the preconcentration and separation of gold at trace levels<sup>11-15</sup>. At this point, graphitized carbon black has been proposed as a novel solid phase extraction sorbents for various inorganic and organic materials at trace levels. They possess excellent adsorption ability because of their large specific surface area<sup>16-18</sup>.

The aim of this work is to develop of a separation and preconcentration method for the determination of gold by FAAS using graphitized carbon black as sorbent and 2-carboxyl-1-naphthalthiorhodanine (CNTR) as complexing agent. The graphitized carbon black tightly adsorbed CNTR and thus, the adsorbed CNTR did not wash away during the elution step. This means that the graphitized carbon black cartridge can be used several times without decreasing the enrichment factor.

### EXPERIMENTAL

Carbopack™ B graphitized carbon black (60-80 mesh) was obtained from Sigma-Aldrich Corporation (USA). All solutions were prepared with double distilled water. Otherwise stated, analytical-grade phosphoric acid and other chemicals were obtained from Merck (Darmstadt, Germany). CNTR solution, 1.0 % (m/v), was prepared by dissolving 0.1 g of the reagent in ethanol.

**Preparation of modified graphitized carbon black cartridge:** In a 50 mL beaker, 10.0 g of graphitized carbon black was added to 10 mL of CNTR ethanol solution (1.0 %) and mixed well. The ethanol was evaporated and the modified graphitized carbon black was obtained. A teflon cartridge (0.8 cm length and 0.5 mm in diameter, Fig. 1) was packed with 0.25 g of the modified graphitized carbon black.

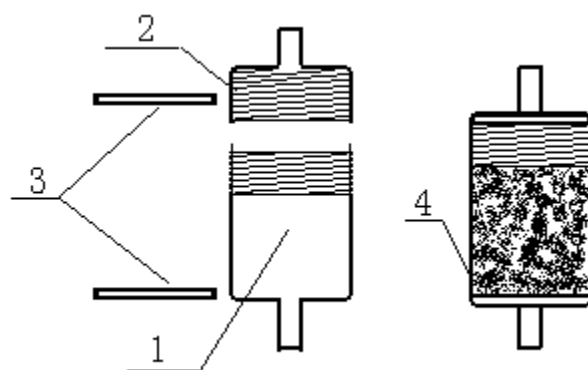


Fig. 1. The SPE cartridge (1) tube for fill in the sorbent, (2) screw cap for sealing the tube), (3) sieve plate, (4) modified graphitized carbon black

**Apparatus:** A Perkin-Elmer model A Analyst 600 atomic absorption spectrometer equipped with a model AS-800 autosampler (Norwalk, CT) and furnished with a gold hollow-cathode lamp was used. The instrument was adjusted according to the standard conditions: Lamp current 4.0 mA, wavelength 242.8 nm, air-acetylene

flame (air flow rate  $6.0 \text{ L min}^{-1}$ , acetylene flow rate  $1.8 \text{ L min}^{-1}$ ), spectral band width  $0.5 \text{ nm}$ . The pH of aqueous solutions was checked using a Beckman F-200 pH meter with a glass electrode.

**Procedure:** The method was tested with model solution before its application to real samples. A 50-1000 mL of Au(III) solution (contain  $0.1 \text{ mol L}^{-1}$  phosphoric acid) was passed through the cartridge at a flow rate of  $10.0 \text{ mL min}^{-1}$ . After finishing the sample solution, a volume of  $2.0 \text{ mL}$  of  $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  solution was passed through the cartridge in the reverse direction at a flow rate of  $2.0 \text{ mL min}^{-1}$  to elute the Au(III) ions. The per cent of metal ions adsorbed on the cartridge for the concentration of Au(III) was calculated from the amount of Au(III) ions in the starting sample and the amount of Au(III) eluted from the cartridge.

For clean water sample determination, the samples were acidified with phosphoric acid (the phosphoric acid concentration in sample was adjusted to  $0.1 \text{ mol L}^{-1}$ ) and the sample solution was passed through the cartridge. Gold ions retained on the cartridge were eluted with  $2.0 \text{ mL}$  of  $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  solution. The eluent was analyzed by the flame atomic absorption spectrometry.

If the organics present in water interfere with the determination, the sample was digested as following procedure: Taking an appropriate volume of sample in a  $500 \text{ mL}$  flask and concentrated the sample to about  $20 \text{ mL}$  by heating on a hot plate. To this solution,  $5.0 \text{ mL}$  of concentrated nitric acid,  $2.0 \text{ mL}$  of concentrated hydrochloric acid and  $5 \text{ mL}$  of 30 % hydrogen peroxide were added. The mixture was heated on hot plate till evaporated to near dryness. The residue was dissolved with  $20 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  of phosphoric acid and afforded to the above preconcentration procedure.

The ore samples for determination were Chinese Certified Reference Standard Material obtained from the Chinese Standard Material Center.

For ore determination, a  $2.0 \text{ g}$  of ore sample is weighed into a  $50 \text{ mL}$  of teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which,  $20 \text{ mL}$  of aqua regia was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001,  $1000 \text{ W}$ , Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for  $0.5 \text{ h}$ . The digested material was evaporated to incipient dryness. Then,  $20 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  phosphoric acid was added and heated close to boiling to leach the residue. After cooled, the residue was filtrated and the undissolved residue was washed with  $0.1 \text{ mol L}^{-1}$  phosphoric acid for 2 times. The leachate was collected into a  $100 \text{ mL}$  of calibrated flask quantitatively and afforded to the above preconcentration procedure.

## RESULTS AND DISCUSSION

2-Carboxyl-1-naphthalthiorhodanine (CNTR) is a spectrophotometric reagent for gold in our laboratory. It can react with gold at room temperature rapidly<sup>12</sup>. CNTR can also be adsorbed on graphitized carbon black surfaces. After the adsorption,

the CNTR on graphitized carbon black is completely stable and does not wash off when using H<sub>2</sub>O or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution as a washing solvent. This means that the graphitized carbon black treated with CNTR can be used several times for separation and preconcentration of Au(III) without decreasing the enrichment factor of the solid phase.

**Optimization of variables:** First of all, to obtain the best quantitative recoveries of Au(III) ions, many parameters such as pH of sample solution, sample volume, the concentration of washing solution, sample flow-rate through the cartridge, capacity of the modified graphitized carbon black and the effect of matrix on the preconcentration step should be studied.

In the optimization steps, 0.25 g of graphitized carbon black was used. The influence of pH of sample solution on the preconcentration step of Au(III) was also studied. Results showed that the optimal condition for the reaction of Au(III) with CNTR is in the acid medium and the phosphoric acid has the best effect. For this purpose, 200 mL of 0.05 µg mL<sup>-1</sup> Au(III) as different phosphoric acid concentration medium were passed through the modified solid phase. Then the Au(III) concentration in eluent solution was checked using FAAS. The results shown that suitable phosphoric acid concentration for adsorption of Au(III) on the modified graphitized carbon black is around 0.05-0.5 mol L<sup>-1</sup>. Therefore, a 0.1 mol L<sup>-1</sup> phosphoric acid medium was used for the preconcentration step.

For eluting the Au(III) from the solid phase, after the extraction of 0.2 mg gold from 200 mL water by the modified cartridge, the Au(III) ion was eluted with various potential eluants. The results are summarized in Table-1. The Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was founded to be the best eluant. The results also shown that it is easier to elute the retained Au(III) in the reverse direction in comparison to the forward direction (Only 2.0 mL of 0.1 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was needed when eluted in reverse direction. However, 8 mL of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was needed when eluted in forward direction). Thus, it is also recommended to invert the cartridge before elution (Fig. 2).

TABLE-1  
EFFECT OF DIFFERENT ELUANT ON THE RECOVERY OF GOLD

	Eluant volume	1 mL	2 mL	3 mL	4 mL	5 mL	6 mL
The recovery of gold (%) using different eluant	HNO <sub>3</sub> (0.02 mol L <sup>-1</sup> )	14.5	26.5	38.5	46.9	54.8	58.9
	HNO <sub>3</sub> (0.1 mol L <sup>-1</sup> )	16.3	31.5	43.6	49.5	57.9	67.7
	HNO <sub>3</sub> (0.5 mol L <sup>-1</sup> )	21.3	38.2	56.9	65.0	76.7	82.1
	Thiourea (0.02 mol L <sup>-1</sup> )	37.8	63.6	91.7	95.7	96.4	98.1
	Thiourea (0.1 mol L <sup>-1</sup> )	40.4	67.9	93.3	96.4	96.6	96.1
	Thiourea (0.5 mol L <sup>-1</sup> )	43.7	72.3	95.7	96.8	97.7	97.4
	EDTA (0.02 mol L <sup>-1</sup> )	6.15	11.5	14.1	18.0	25.0	27.1
	EDTA (0.1 mol L <sup>-1</sup> )	7.82	14.3	18.5	22.2	28.7	34.1
	EDTA (0.5 mol L <sup>-1</sup> )	10.4	17.1	24.3	29.6	36.2	44.4
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.02 mol L <sup>-1</sup> )	67.1	91.6	93.1	94.0	95.6	96.7
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1 mol L <sup>-1</sup> )	72.0	96.2	97.5	96.8	-	-
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.5 mol L <sup>-1</sup> )	78.8	96.8	97.5	98.4	-	-

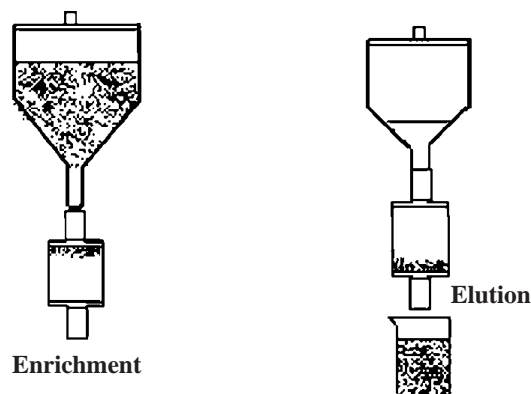


Fig. 2. Eluting the gold in the reverse direction

The influence of the sample flow rate on preconcentration efficiency of Au(III) ions through the cartridge was also investigated. For this purpose, a volume of 50 mL of  $0.2 \mu\text{g mL}^{-1}$  Au(III) solution (contain  $0.1 \text{ mol L}^{-1}$  phosphoric acid) was passed through a series of cartridge at different flow rates. Then the adsorbed Au(III) was washed with 2.0 mL of  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  solution and the Au(III) content was measured using FAAS. The results showed that using a sample flow rate over  $12 \text{ mL min}^{-1}$  can caused a decrease of the Au(III) ions recoveries. Therefore, a sample flow rate of  $10.0 \text{ mL min}^{-1}$  was used for further studies.

The effect of flow rate of eluant on desorption efficiency of Au(III) ions from the cartridge was also checked in the range of  $1.0\text{-}5.0 \text{ mL min}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  solution. The results showed that the recovery of gold was maximized when using elution rates up to  $1.0\text{-}2.5 \text{ mL min}^{-1}$ . Therefore,  $2.0 \text{ mL min}^{-1}$  was selected.

The capacity of the modified graphitized carbon black for adsorption of Au(III) was checked by passing 150 mL of Au(III) solution containing  $0.05\text{-}10 \mu\text{g mL}^{-1}$  Au(III) through the cartridge (containing 0.25 g modified graphitized carbon black). The metal ions were stripped off the modified graphitized carbon black with 2.0 mL  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  solution and measured by FAAS. Under the condition of gold recovery  $\geq 95 \%$ , the adsorption capacity was calculated to be  $0.75 \text{ mg g}^{-1}$ . The cartridge has adequate capacity to enrich the gold in real sample.

Reusability of the modified graphitized carbon black was checked using the same solid phase for sorption-desorption of Au(III) ions for 50 times the reusability was tested. The maximum change in the performance (sorption capacity) of the solid phase after the repeated use was less than 2 %, indicating that its repeated use is feasible as leaching of the dye from the graphitized carbon black matrix is insignificant. No change in the sorption capacity of the modified graphitized carbon black was noticed after storing it for 5 months.

**Calibration graphs and detection limits:** Under the FAAS analysis conditions, regression equations of metal ions were established based on the standard samples injected and their absorption signals. The results shown that the linearity range for

gold was obeyed in the range of 0.01-3.5  $\mu\text{g mL}^{-1}$  and the linear regression equation obtained was:  $A = 0.421 + 0.0186 C (\mu\text{g mL}^{-1})$ ,  $r = 0.9994$ .

The results showed that the limit of quantitative preconcentration was 0.2  $\mu\text{g L}^{-1}$  Au(III) with a preconcentration factor of 500 (1000 mL of sample solution was passed the cartridge). Recoveries from further diluted solutions or larger sample volume were not quantitative (the recovery of gold < 95 %). The limit of detection values based on 3 times the standard deviations of the blank was equal to 0.05  $\mu\text{g L}^{-1}$  Au(III).

**Interference study:** The influence of matrix ions in water samples on the separation and recovery of Au(III) ions was also investigated by passing different amounts of potential interfering ions plus 50.0  $\text{ng mL}^{-1}$  Au(III). The results showed that 10000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen carbonate, carbonate and sulfate, 500-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), Pb(II), did not interfere. The results confirm that the modified solid phase is highly selective for Au(III) and interferences did not occur.

**Application to real samples:** The method was applied to the determination of gold in water and ore. The results (deducted the reagents blank) were given in Table-2. A standard method using ICP-MS had also been used as reference method and the result were also shown in Table-2.

TABLE-2  
DETERMINATION OF GOLD IN THE WATER AND ORE SAMPLES

Samples	ICP-MS method	Proposed method	RSD % (n = 7)	Recovery (%) (n = 5)
River water	6.140 ( $\mu\text{g L}^{-1}$ )	6.220 ( $\mu\text{g L}^{-1}$ )	3.2	88-96
Planting effluents	22.100 ( $\mu\text{g L}^{-1}$ )	21.200 ( $\mu\text{g L}^{-1}$ )	2.8	93-97
Ore <sup>†</sup> (GBW(E) 070012)	0.336 ( $\text{g T}^{-1}$ )	0.312 ( $\text{g T}^{-1}$ )	3.3	93-102
Ore <sup>‡</sup> (GBW(E) 070014)	3.100 ( $\text{g T}^{-1}$ )	3.220 ( $\text{g T}^{-1}$ )	2.7	94-104

<sup>†</sup>Certified value:  $0.3 \pm 0.02 \text{ g T}^{-1}$ ; <sup>‡</sup>Certified value:  $3.14 \pm 0.06 \text{ g T}^{-1}$

## Conclusion

The method could be applied for the separation, preconcentration and selective determination of trace amounts of gold(III) as low as 0.05  $\mu\text{g L}^{-1}$ . The modified graphitized carbon black is stable for several treatments of sample solutions without the need for using any chemical reagent. For real samples determination, the relative standard deviations were below 3.3 % and the recoveries of Au(III) were in the range of 88-104 %. The recoveries obtained by the present solid phase are also comparable with the widely used and recently reported chelating resins. Under the optimum conditions, gold in aqueous samples was concentrated about 500-fold. This method is high times enrichment factor. The obtained results are in good agreement with the certified values and the reference method, which proved the applicability of the developed method to the quantitative separation/ preconcentration of gold in

the water and ore. The lower acid concentration required for desorption of metal ion avoids the requirement of further dilution for AAS measurement and is among the advantage of the modified graphitized carbon black, which also is not affected by leaching problems.

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### REFERENCES

1. H. Schmidbaur, S. Cronje, B. Djordjevic and O.U. Schuster, *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. K. Pyrzynska, *Spectrochim. Acta. B*, **60**, 1316 (2005).
4. R.R. Barefoot, *Anal. Chim. Acta*, **509**, 119 (2004).
5. K.E. Jarvis, J.G. Williams, S.J. Parry and E. Bertalan, *Chem. Geo.*, **124**, 37 (1995).
6. A. Scheffer, C. Engelhard, M. Sperling and W. Buscher, *Anal. Bioanal. Chem.*, **390**, 249 (2008).
7. M.S. El-Shahawi, A.S. Bashammakha and S.O. Bahaffia, *Talanta*, **72**, 1494 (2007).
8. M. Soylak and M. Tuzen, *J. Hazard. Mater.*, **152**, 656 (2008).
9. M. Shamsipur and M. Ramezani, *Talanta*, **75**, 294 (2008).
10. H.B. Senturk, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, L. Elci and M. Tufekci, *J. Hazard. Mater.*, **149**, 317 (2007).
11. K. Pyrzynska and M. Trojanowicz, *Crit. Rev. Anal. Chem.*, **29**, 313 (1999).
12. Z.Y. Chen, Z.Y. Huang, J. Chen, Q.F. Hu, J.Y. Yin, Q.D. Su and G.Y. Yang, *Anal. Lett.*, **39**, 579 (2006).
13. L. Elci, D. Sahan, A. Basaran and M.S. Soylak, *Environ. Monitor. Assess.*, **132**, 331 (2007).
14. E.A. Moawed, *Anal. Chim. Acta*, **580**, 263 (2006).
15. Q.F. Hu, G.Y. Yang, Y.Y. Zhao and J.Y. Yin, *Anal. Bioanal. Chem.*, **375**, 831 (2003).
16. H. Sabik and R. Jeannot, *J. Chromatogr. A*, **879**, 73 (2000).
17. O. Shimelis, Y.H. Yang, K. Stenerson, T. Kaneko and M. Ye, *J. Chromatogr. A*, **1165**, 18 (2007).
18. Y. Song, S. Zhao, P. Tchounwou and Y.M. Liu, *J. Chromatogr. A*, **1166**, 79 (2007).

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