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Contributed Paper

Determination of Gold by FAAS After Solid Phase Extraction on Freshly Precipitated Copper piperazine dithiocarbamate

Hasan Cesur* and Vildan Aksu

Department of Chemistry, Faculty of Art and Science, Ondokuz Mayıs University, Samsun, 55139, Turkey.

*Author for correspondence; e-mail: hasanc@omu.edu.tr

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ABSTRACT

A new solid phase extraction (SPE) procedure was developed for the pre-concentration of Au(III) ions in aqueous system prior to its determination by flame atomic absorption spectrometry (FAAS). For this purpose, freshly precipitated metal-piperazinedithiocarbamates (Mn(PDTC), Zn(PDTC), Cd(PDTC), Fe₂(PDTC)₃, Co(PDTC), Cu(PDTC), Ni(PDTC), Pb(PDTC), Hg(PDTC) and Au₂(PDTC)₃) were synthesized and they have been tested for the extraction of their metal ions in aqueous solution. The freshly precipitated Cu(PDTC) was selected for the pre-concentration of Au(III) in aqueous system and the optimum experimental conditions for the quantitative sorption of Au(III) such as pH, effect of aqueous phase volume, effect of extraction period and the effect of diverse ions on the sorption of Au(III) have been investigated. The linearly range (0.5-5 mg L⁻¹), regression equation ($y = 0.0141X - 0.0005$), correlation coefficient ($r^2 = 0.9982$), detection limit (3.6 µg L⁻¹) and determination limit (11.3 µg L⁻¹) in final Au(III) solution were obtained. The proposed method has been applied for the determination of Au(III) in some real samples.

Keywords: solid phase extraction (SPE), piperazinedithiocarbamate, gold determination, AAS

1. INTRODUCTION

Gold is an important noble metal and its concentration in natural environment, basic rocks and soils is very low. Therefore, pre-concentration and separation are necessary prior to determination by atomic absorption spectrometry (AAS). A lot of methods: solid phase extraction (SPE) [1-4], dispersive liquid-liquid micro extraction (DLLME) [5, 6], cloud point extraction (CPE) [7, 8] and co-precipitation [9-11]

have been applied for this purpose. Among the methods SPE enjoys a favoured position because of its simplicity, speed, and wide scope. Selective extraction of the metal ion depends on chelates and the chelating agents play a very important role in SPE procedure.

In recent years, the dithiocarbamate SPE procedure has been applied to solid phase extraction of some trace metal ions

prior to determination by AAS [12-16]. The most important reagents for this work are sodium diethyldithiocarbamate and ammonium pyrrolidine dithiocarbamate. In the usual dithiocarbamate SPE methods, a dithiocarbamate reagent is added to a sample solution, and then formed metal-dithiocarbamate complexes are extracted on a solid material, such as microcrystalline naphthalene, silica gel, amberlite XAD resins and activated carbon. After that the metals are eluted with a solution and measured by AAS.

Dithiocarbamate reagents also have been used for co-precipitation method to pre-concentrate trace metals [11, 17-18]. In this method a lot of metal ions simultaneously precipitate with a carrier metal-DTC and selectivity cannot be achieved.

In our previous studies, some metal-dithiocarbamates immobilized on adsorbent such as activated carbon [19], microcrystalline naphthalene [20] were studied for extraction of Cu(II), Ni(II), Cd(II) ions in different samples prior to their determination by FAAS.

Recently, a new technique was developed in dithiocarbamate SPE procedure. In this method freshly precipitated metal diethyldithiocarbamate complexes, were used for the adsorption of metal ions in aqueous system. In these works freshly precipitated metal (Mn, Zn, Cd, Fe, Co, Cu, Ni, Pb, and Hg) diethyldithiocarbamate complexes, have been studied as reagents for the selective extraction of aqueous Mn(II), Zn(II), Cd(II), Fe(III), Co(II), Cu(II), Ni(II), Pb(II), and Hg(II) ions. It was found that these reagents show excellent selectivity for the extraction of the investigated metal ions [21-24].

Diethyldithiocarbamate reagent are very unstable even in weakly acidic medium and they are therefore of limited

value in acid solutions. Therefore, the piperazinedithiocarbamate is more suitable than diethyldithiocarbamate. If the piperazinedithiocarbamate is used in acidic medium, its stability is much higher. Since piperazinedithiocarbamate has two $-CS_2$ groups its metal chelates are polymeric, stable and insoluble in dilute acidic solutions. In this study piperazinedithiocarbamate was selected as a chelating reagent.

Au(III) ions was not studied dithiocarbamate SPE procedure until this time. Moreover gold samples are highly acidic. On the other hand, the choice of the freshly precipitated metal piperazinedithiocarbamate is also a very important. Stability of the metal piperazinedithiocarbamates decreases as the following order: Au, Hg, Cu, Pb, Ni, Cd, Fe, Co, Zn, and Mn. Therefore, Hg piperazinedithiocarbamate is more suitable than others from the point of selectivity. But, all Hg compounds are very toxic and harmful to health. In this present study, taking into account environmental and health freshly precipitated Cu(PDTC) were selected. Using the freshly precipitated Cu(PDTC) a SPE method was developed for the pre-concentration of Au(III) ions in aqueous solution prior to its determination by FAAS. The optimal experimental conditions for the quantitative adsorption of Au(III) has been investigated.

2. MATERIALS AND METHODS

2.1 Apparatus and Reagents

Metal concentration measurements were determined by a UNICAM 929 FAA spectrophotometer. It is equipped with 5 cm burner head and a single hollow cathode lamp. pH measurements were carried out by a JENWAY 3040 model pH-meter. Piperazine and $HAuCl_4$ (1000 mgL^{-1} stock solution) was purchased from Merck. Stock solutions of the metal ions ($0.1\ mol\ L^{-1}$)

were prepared with their nitrate salts.

2.2 Test Procedure

Synthesis of potassium piperazine dithiocarbamate: The piperazinedithiocarbamate was synthesized according to a modified method given in the literature [19]. The solution of KOH (0.1mol) was added to a piperazine solution (0.2 mol) in a diethyl ether at 0 °C. CS₂ (0.1mol) was added drop wise to this solution in a water ice bath at about 0 °C. The mixture was stirred for 60 min, then the aqueous phase was separated and it was used in the synthesis of metal-PDTC complexes.

Synthesis of metal complexes of PDTC: The piperazinedithiocarbamate solution and the metal solution in water were

mixed in stoichiometric ratio. One by one the metal-PDTC's (Mn(PDTC), Zn(PDTC), Cd(PDTC), Fe₂(PDTC)₃, Co(PDTC), Cu(PDTC), Ni(PDTC), Pb(PDTC), Hg(PDTC) and Au₂(PDTC)₃) were precipitated in the solution. They were filtered and washed with deionized water several times. The solid products were stored in a flask for the SPE procedure.

SPE procedure: A 30 mL of metal solution (containing 5.0 mg L⁻¹) was taken, 2.0 mL of acetate buffer solution and 0.20 g of freshly precipitated-metal-PDTC were added. The mixture was shaken for 10 min. After that, the solution was filtered and the metal concentrations were determined by FAAS. The results of SPE efficiencies are presented in Table 1.

Table 1. SPE of metal ions by different metal-PDTC precipitants.

	Mn ²⁺	Zn ²⁺	Co ²⁺	Fe ³⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cu ²⁺	Hg ²⁺	Au ³⁺
Mn-PDTC		+	+	+	+	+	+	+	+	+
Zn-PDTC	-		+	*	+	+	+	+	+	+
Co-PDTC	-	-		*	-	-	-	*	+	+
Fe ₂ (PDTC) ₃	-	-	-		*	+	*	+	+	+
Cd-PDTC	-	-	-	-		-	*	+	+	+
Ni-PDTC	-	-	-	-	-		*	+	+	+
Pb-PDTC	-	-	-	-	-	-		+	+	+
Cu-PDTC	-	-	-	-	-	-	-		+	+
Hg-PDTC	-	-	-	-	-	-	-	-		+
Au ₂ (PDTC) ₃	-	-	-	-	-	-	-	-	-	-

+, mean of the extraction efficiency (> 99%)

*, mean of the extraction efficiency (30-80%)

-, mean of the extraction efficiency (< 1%)

2.3 Application to Real Samples

A gold solution, 2 mL of acetate buffer solution and 0.20 g of freshly precipitated Cu(PDTC) were mixed in an Erlenmeyer flask. The mixture was stirred vigorously and then it was filtered. Solid product containing Au(III) was dissolved with HNO₃-HCl mixture (1/3 v/v) and gold

concentration was determined by FAAS.

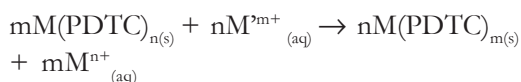
3. RESULTS AND DISCUSSIONS

3.1 Solid-phase Extractions

Synthesized the freshly precipitated metal-piperazinedithiocarbamate (PDTC) reagents; Mn(PDTC), Zn(PDTC), Cd(PDTC), Fe₂(PDTC)₃, Co(PDTC),

Cu(PDTC), Ni(PDTC), Pb(PDTC), Hg(PDTC) and Au₂(PDTC)₃ were tested extraction of their metal ions in aqueous system. By using exchange reactions the following increasing stability order of metal piperazinedithiocarbamates was found: Mn(II), Zn(II), Co(II), Fe(III), Cd(II), Ni(II), Pb(II), Cu(II), Hg(II) and Au(III). The metal piperazinedithiocarbamates with the lower stability can be selectively extracted all other metal ions with higher stability their chelates. Thus for instance gold can completely displace Mn(II), Zn(II), Co(II), Fe(III), Cd(II), Ni(II), Pb(II), Cu(II) and Hg(II) from their piperazinedithiocarbamates. If the Cu(PDTC) is used in solid phase extraction procedure, gold extraction selectivity is much higher.

The mechanism of the metal adsorption on freshly precipitated dithiocarbamate was discussed [25]. Freshly precipitated metal-piperazinedithiocarbamates selectively extract the metal ions by exchange reaction:



The stability series of the piperazinedithiocarbamates was found: Au, Hg, Cu, Pb, Ni, Cd, Fe, Co, Zn, and Mn (Table 1.) It is similar to the metal-diethyldithiocarbamates [25]. In the SPE procedure, a metal-PDTC in the series can extract only when it's on the right metal ion. Thus, selective extraction of the metal ions can be carried out.

Formerly, dithiocarbamate liquid-liquid extraction method were studied by some authors and the Log K_{ex} of value of metal-diethyldithiocarbamate has been presented in the literature (Log K_{ex} values: 68.2 (Au), 44.4 (Hg), 26.1 (Cu), 24.0 (Ni), 20.2 (Pb), 17.8 (Cd), 14.7 (Co), 15.4 (Zn),

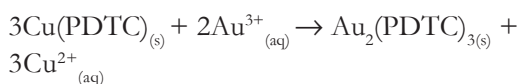
13.4 (Fe) and 8.0 (Mn)) [27, 28]. The stability series of the metal-PDTC is similar to the extraction constant series of the metal-diethyldithiocarbamate.

The proposed SPE procedure is more advantageous than traditional dithiocarbamate SPE. Give an evidence in favour of the statement, in this system, selective extractions of the metal ions are carried out easily.

The proposed SPE method in comparison with co-precipitation technique is more useful in terms of metal ion selectivity. Moreover, in co-precipitation technique numerous diverse matrix anions are adsorbed in co-precipitation procedure.

3.2 SPE of Gold

The stability constant of Cu(PDTC) is lower than Au₂(PDTC)₃ and Au(III) replace with Cu(II) on freshly precipitated Cu(PDTC)₂.



Then, solid Cu(PDTC) (adsorbed Au(III)) is dissolved with HNO₃-HCl mixture and gold is determined by FAAS. For the pre-concentration of Au(III) the optimal conditions were also studied.

3.3 Effect of pH

A 30.0 mL of gold solution (5 mg L⁻¹ Au(III)) was taken. To adjust the pH HNO₃-KOH solutions were added. 0.20 g of FP Cu(PDTC)_(s) was added as a solid adsorbent. The solution was stirred for 10 min. After this period, it was filtered and gold concentration was determined by FAAS. The recoveries were presented in Figure 1. Optimum pH 5-6 was chosen and acetate buffer solution was used for this purpose.

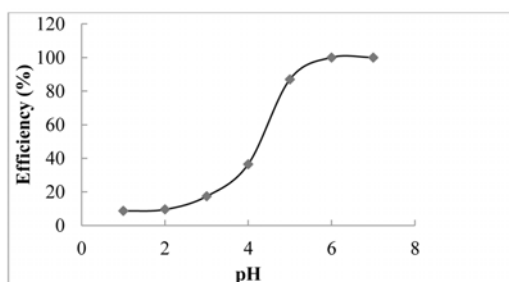


Figure 1. The effect of pH SPE of Au(III), Au(III) concentration: 5 mg L⁻¹, sample volume: 30.0 mL, the amount of FP Cu(PDTC): 0.20 g, and extraction period: 10 min.

3.4 Effect of Extraction Period

Extraction period is an important parameter for extraction of metal ions. A 30.0 mL gold solution (5 mg L⁻¹ Au(III)) was taken and proposed SPE method was applied at various period. As shown in Figure 2, the results were indicated that Au(III) extraction was quantitatively finished with for 10 min. Therefore, the extraction time of 10 min was selected for further works.

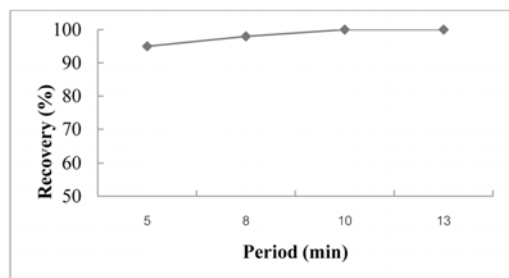


Figure 2. Effect of extraction period, pH: 6.0, Au(III) concentration: 5 mg L⁻¹, sample volume: 30.0 mL, and the amount of FP Cu(PDTC): 0.20 g.

3.5 Effect of Aqueous Phase Volume

An Au(III) solution (5 mgL⁻¹ Au(III)) was taken and aqueous phase volume was varied from 30 mL to 1000 mL by distilled water. Au(III) concentrations was determined according to the proposed SPE method. The results given in Figure 3, showed that Au(III) extraction was attained with 1000 mL.

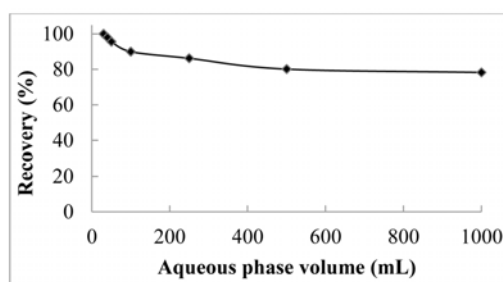


Figure 3. Effect of volume aqueous phase, pH: 6.0, Au(III) concentration: 5 mg L⁻¹, sample volume: 30.0 mL, the amount of FP Cu(PDTC): 0.20 g, and finally solution volume: 30.0-1000.0 mL.

3.6 Effect of Diverse Ions

Gold determination is too difficult in soil, mineral, alloy or other samples because of the high concentrations of matrix elements. (such as Fe, Zn, Ag, Pb, Zn, Na, K, Ni and Cr). Therefore, the matrix solutions were prepared the amount of gold and mixed together with matrix metals. The gold solution of 30 mL containing 5 mg L⁻¹ Au(III) and different metal salts was mixed and gold concentrations were carried out by the proposed SPE method. The results given in Table 2, showed that Au(III) was separated from other matrix metals.

Table 2. Effect of diverse ions for the determination of gold.

Diverse Ion	Tolerance Limit* (g/L)
Fe ³⁺	4.6
Zn ²⁺	>10
Ag ⁺	4.6
Pb ²⁺	5
Cu ²⁺	>10
Mg ²⁺	9.1
Ni ²⁺	>10
Cr ³⁺	9.1
Na ⁺	>10
K ⁺	>10
NO ₃ ⁻	4.6
Cl ⁻	>10
CN ⁻	>10

*Tolerance limit was taken as the amount causing an error of $\pm$ % 5 in absorbance.

3.7 Effect of Amount of Cu(PDTC)

The effect of the quantities of Cu(PDTC) on the pre-concentration of Au(III) were investigated. For this purpose a 30.0 mL gold solutions (5 mg L^{-1} Au(III)) was taken and 0.05-0.30 g of Cu(PDTC) was added. The proposed method was applied and gold concentrations were determined. The results given in Figure 4. showed that quantitative extraction of Au(III) was carried out with 0.10 g of FP Cu(PDTC). The optimum amount of Cu(PDTC) was taken as 0.20 g for further experiments.

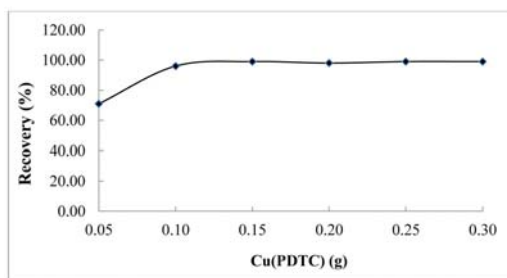


Figure 4. Effect of the amount of Cu(PDTC), pH:6.0, Au(III) concentration: 5 mg L^{-1} , sample volume: 30.0 mL, extraction period: 10 min., and the amount of FP Cu(PDTC): 0.05-0.30 g.

3.8 Validation of the Method

Under the optimized conditions, different standard solutions of Au(III) ($0.1\text{-}10 \text{ mg L}^{-1}$ Au(III)) was taken and proposed SPE method was applied. A graph was constructed with ten results (Figure 5) according to the general procedure. Linearity was maintained in the range of $0.5\text{-}5 \text{ mg L}^{-1}$ for Au(III) final solutions. The regression equation ($y = 0.0141X - 0.0005$) and the coefficient ($r^2 = 0.9982$) were obtained with the method of least squares.

The limit of detection (LOD) and the limit of quantification (LOQ) of Au(III) ions were calculated for optimal experimental conditions. The LOD ($3.6 \text{ }\mu\text{g L}^{-1}$) and the LOQ ($11.3 \text{ }\mu\text{g L}^{-1}$) for Au(III) based on the

concentration corresponding three times and ten times the standard deviations of the blank signal ($N = 10$), respectively. The recovery of the method (94.2) and RSD (8.7%) were also calculated.

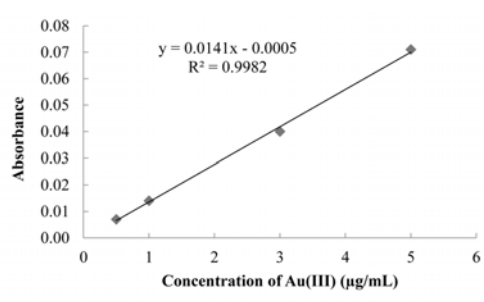


Figure 5. Calibration curve, pH:6.0, Au(III) concentration: 0, 5-5, 0 mg L^{-1} , sample volume: 30.0 mL, the amount of FP Cu(PDTC): 0.20 g, and extraction period: 10 min.

3.9 Determination of Gold in Certificate Material

The proposed SPE method was tested to the determination of Au(III) in certificated reference material solution. (Massive sulphide with gold and platinum groups element, SRM PR3 WMS-1a, , Fe: 45.4%, S: 28.17%, Ca: 3.09%, Ni: 3.02%, Cu: 1.40%, Al: 1.35% Au: $0.30 \text{ }\mu\text{g g}^{-1}$, Pd: $1.45 \text{ }\mu\text{g g}^{-1}$, Pt: $1.91 \text{ }\mu\text{g g}^{-1}$). 10.00 g of the material was taken in a 50 mL Erlenmeyer flask and HCl and HNO_3 solution was added. The mixture was heated until to dryness. The residue was cooled and dissolved in dilute HNO_3 solution. The pH of the solution was adjusted by acetate buffer, gold was determined proposed SPE method. The results were given in Table 3. The results are in good agreement with the certified value.

3.10 Determination of Gold in Various Samples

Two samples consisting of gold was obtained from ETI Copper Plant in Samsun,

Turkey. 5.000 g of the sample was taken and dissolved with HNO_3 -HCl. Gold concentrations were determined by proposed SPE method. The results were given in Table 4.

Table 3. Determination of Au(III) in certified material.

SRM	Certified value ($\mu\text{g/g}$)	Found ($\mu\text{g/g}$)*	Recovery, RSD
PR03 WMS-1a Massive sulphide with gold and platinum groups element	0.30	0.28 ± 0.02	94.2 ± 8.7

*Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

Table 4. Determination of Au(III) in various samples.

Samples (obtained from ETI Copper Plant in Samsun, Turkey)	Au (mg/Kg)*
Sample 1 (Consantre copper)	4.08 ± 1.73
Sample 2 (Mat copper)	6.74 ± 0.42

*Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

4. CONCLUSIONS

Gold is one of the rarest elements in environments. It is frequently determined by AAS in various samples. Generally, a pre-concentration or separation is necessary in sapling procedure. The extraction of gold plays very important role in this procedure because of its speed, versatility, simplicity and selectivity. SPE is a simple and useful technique for the pre-concentration of the metal ions. In this work, it is observed that the freshly precipitated Cu(PDTC) can be used for the selective extraction of Au(III) from aqueous solution without an adsorbent.

According to this results, using the different metal-dithiocarbamates, hydroxides, sulfides etc. the metal ions can be extracted selectively from aqueous solution. The new methods can be developed for their pre-concentration.

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