

Selective Separation, Preconcentration, and Determination of Au(III) Ions in Environmental Samples by Coprecipitation With a 1,2,4-Triazole Derivative

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INTRODUCTION

Gold, a precious pliable metal, has played a conspicuous part in most of the known ancient cultures as a gauge of economic value and material for costly works of art (1,2). The metal is used in jewelry but also widely in other industries such as medicine, plating, electronics, as well as for coating certain space satellites. Gold occurs in very low concentrations in basic rocks, soils, and the open sea, and averages about 4.0 ng g⁻¹, 1.0 ng g⁻¹, and 0.05 µg L⁻¹, respectively (3-5).

Although there are a number of modern instrumental analytical techniques, quantitative analysis of metal ions is carried out by flame atomic absorption spectrometry (FAAS) due to its relative ease of operation, low instrument cost, selectivity, low detection limits, and applicability to a wide range of elements (6-8).

In many cases, the available instrumental techniques with their various refinements do not have the required sensitivity or freedom from matrix effects and, therefore, cannot be used for direct analysis. Consequently, a need has been created to increase the relative concentration of trace metals with respect to the main components in the sample to ensure accurate and reliable measurements (5,8). The development of separation and preconcentration methods for the

ABSTRACT

An effective, simple, low-cost, and accurate separation and preconcentration procedure which has minimal impact on the environment has been developed. It is based on the carrier element-free coprecipitation (CEFC) of Au(III) ions using N-benzyl-2-([3-methyl-4-(2-morpholine-4-ylethyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazole-1-yl]acetyl)hydrazinecarboxamide (BODAH) as an organic coprecipitant.

Determination of the Au(III) ion levels was performed by flame atomic absorption spectrometry (FAAS). The developed method provided a detection limit of 0.36 µg L⁻¹ and the relative standard deviation for Au(III) ions was found to be 5.1%. Spike tests and certified reference material analyses were performed to validate the method.

The developed method was systematically investigated in different sets of experimental parameters that influence the quantitative recovery of the Au(III) ions. Based on these investigations, the optimum conditions for the determination of Au(III) ions at trace levels were established. The coprecipitation method was applied to anodic slime, gold ore, soil, and water samples to determine their Au(III) levels.

determination of metals at trace levels has helped to solve the problems arising in connection with metallurgy, geology, environmental research, and the life sciences (3). The methods developed for that purpose are based on ion exchange (9), membrane filtration (10), solid phase extraction (11), fire assay (12), cloud point extraction (13), liquid-liquid microextraction (14), and electroanalytical techniques (15).

Coprecipitation, among the other methods mentioned above, is the most preferred since it is cost-effective, user-friendly, has a high pre-concentration factor, requires a short analysis time, and can be applied for separation and preconcentration purposes simultaneously. There are many organic and inorganic coprecipitants that can be employed as efficient coprecipitating agents in the same batch to preconcentrate and separate a variety of analyte ions (16-18). Metal hydroxides and phosphates are the favored inorganic coprecipitants (19), while acetohydrazide derivative (18), pyrrolidine dithiocarbamate (20), and N-cetyl N,N,N-trimethyl ammonium bromide (21) have been used as organic coprecipitants to preconcentrate trace metal ions in aqueous media. In order to obtain a good precipitate, large amounts of a carrier element are used in the medium which may interfere with the preconcentration step. In the "carrier element-free coprecipitation (CEFC)" method, only an organic ligand is used to form a precipitate. The CEFC

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method is preferred among the methods developed for similar purposes since there is no risk of contamination and background adsorption (22).

This paper is devoted to evaluating the separation and preconcentration conditions of Au(III) ions by using N-benzyl-2-[[3-methyl-4-(2-morpholine-4-ylethyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazole-1-yl]acetyl]hydrazinecarboxamide (BODAH) as an organic coprecipitating agent without using a carrier element prior to their flame atomic absorption spectrometric (FAAS) determinations. The influences of various analytical parameters such as pH of the aqueous solution, quantity of BODAH, sample volume, standing time, centrifugation rate and time were investigated on the recovery of the Au(III) ions. The method was also validated by analyzing a certified reference material and performing spike tests. The procedure was then applied to the preconcentration, matrix separation, and determination of Au(III) ions in anodic slime, gold ore, soil, and water samples.

EXPERIMENTAL

Instrumentation

Au(III) ion concentrations were determined using a PerkinElmer® AAnalyst™ 400 atomic absorption spectrometer, equipped with a 10-cm air/acetylene burner head and deuterium background correction (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating conditions are listed in Table I. The pH measurements were made with a Hanna pH-211 digital pH meter (HANNA Instruments, Romania), equipped with a glass electrode. The centrifugation of the solutions was performed using a Sigma 3-16P centrifuge (Sigma Laborzentrifugen GmbH, Germany). The solid samples were digested in a Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) (Milestone Inc., Italy).

Reagents and Solutions

Unless otherwise noted, all reagents were used as received from the manufacturer (E. Merck, Darmstadt, Germany or Fluka, Buchs, Switzerland). All of the solutions were prepared in distilled/deionized water. The standard and working solutions of the Au(III) ions were prepared daily by dilution of the stock solutions of H(AuCl₄).

BODAH (Figure 1), which was used for the first time for an analytical application in this study, was synthesized according to the procedure provided in the literature (23). A 0.3% (w/v) BODAH solution was prepared by dissolving it in ethyl alcohol. The certified reference material, CRM-SA-C Sandy Soil C standard, was procured from High-Purity Standard Inc. (Charleston, SC, USA)

Model Studies for Coprecipitation

In the present study, 50.0 mL of an aqueous solution containing 4.0 µg of Au(III) ions was placed in a centrifuge tube and the pH of the solution adjusted to 3.5. The pH adjustments were carried out either by diluted HCl or NaOH solutions. Then 6.0 mg of coprecipitating agent (2 mL, 0.3%, w/v) was added and the mixture allowed to stand for 30 minutes. This solution was centrifuged at 2500 rpm for 5 minutes to remove the supernatant. The precipitate adhering to the tube was dissolved in 1.0 mL of concentrated HNO₃. The final solution was brought to 2.0 mL volume with distilled/deionized water and the Au(III) ions were determined by FAAS.

TABLE I
Instrumental Operating Conditions

Instrument	PerkinElmer® AAnalyst™ 400 FAAS
Element	Au (III)
Wavelength	242.80
Slit Width	2.7 nm
Lamp applied current	10 mA
Acetylene flow rate	2.5 L min ⁻¹
Air flow rate	10.0 L min ⁻¹

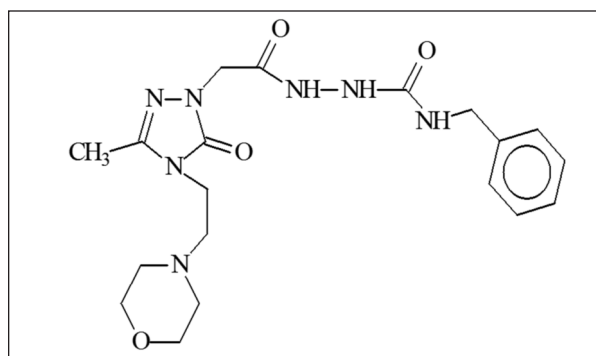


Fig. 1. Chemical structure of BODAH.

Analysis of Real Samples

The present separation and preconcentration procedure was applied to determine the levels of Au(III) ions in seawater (Black Sea, Trabzon, Turkey) and stream water (Şana Stream, Trabzon, Turkey). For that purpose, the water samples were filtered through a cellulose membrane filter of 0.45 µm pore size. After acidification with 1% nitric acid solution, they were stored at 4 °C in a refrigerator in polyethylene bottles. Before the experiments, the pH of the samples was adjusted to 3.5. After addition of the required amount of BODAH, the recommended procedure (as pointed out in the "Model Studies for Coprecipitation" section) was applied.

The solid samples (anodic slime, gold ore, and soil) were microwave digested prior to the application of the present separation and preconcentration procedure. For that purpose, 0.100 g of anodic slime and gold ore, 0.750 g of soil, and 0.250 g of CRM-SA-C Sandy Soil C were weighed into separate Teflon® vessels. Then, 4.5 mL of HCl, 1.5 mL of HNO₃, 1 mL of HF, and 2 mL of H₂O₂ were added to the vessels. The digestion of the solid samples by microwave radiation was performed in four steps: 6 minutes for 250 W, 6 minutes for 400 W, 6 minutes for 650 W, and 6 minutes for

250 W. During these microwave irradiations, the pressure was kept at 45 bars and the ventilation was 3 minutes. At the end of the microwave digestion, the sample volume was brought to 50 mL with distilled/deionized water and then the method was applied.

RESULTS AND DISCUSSION

Optimization Parameters

The effects of pH on the recoveries of Au(III) ions were examined in the solution pH range of 1.0–10.0. As is seen from Figure 2, the quantitative recovery values (>95%) were obtained for Au(III) ions in the pH range of 3.0–4.0, and the pH of 3.5 was selected for all further experiments.

To evaluate the impact of the quantity of BODAH on the coprecipitation of the Au(III) ions, the experiments were carried out with different BODAH amounts ranging from 0.0–12.0 mg [(0–4.0 mL, 0.3% (m/v))]. It was observed that the recovery yields of the Au(III) ions increased with an increase in the quantity of the coprecipitating agent BODAH up to a certain level. The yield of the recoveries for the Au(III) ions were not quantitative (31%) when BODAH was not added to the solution. As shown in Figure 3, the recovery values increased rapidly by increasing the quantity

of BODAH up to 6.0 mg (2 mL, 0.3%, w/v); after that value, there was no change in the recovery yields. On this basis, 6.0 mg of BODAH was added to the solutions in all subsequent work.

The sample volume is one of the most important analytical parameters for obtaining a high preconcentration factor in the determination of metal concentrations of real samples. For this purpose, the effect of sample volume on the quantitative recoveries of the Au(III) ions was investigated in the sample volume ranging from 50–1250 mL. The recovery values decreased with an increase in the volume of the sample solution (Figure 4). Since the recoveries decreased considerably after reaching 750 mL sample volume, this sample volume was applied in the application of the procedure for the analysis of sea and stream waters. The preconcentration factor was calculated by the ratio of the highest sample volume (750 mL) and the lowest final volume (2 mL), which was found as 375 mL.

The effects of standing time and centrifugation time and rate on the recovery of the Au(III) ions were also investigated because these are the important factors affecting the formation and quality of the precipitate. Based on this, the presented coprecipitation procedure was also

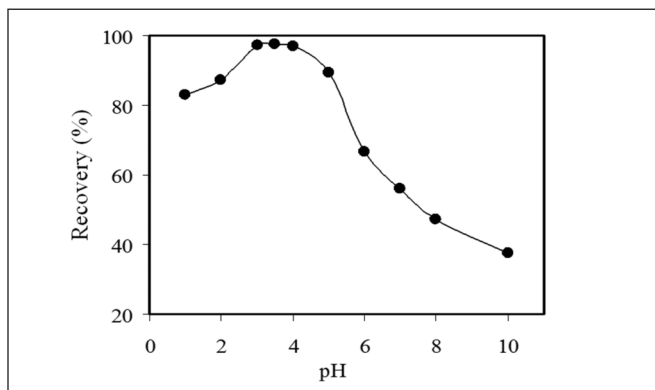


Fig. 2. Effect of pH on the recovery of Au(III) ions (N: 3, sample volume: 50 mL, quantity of BODAH: 6.0 mg, standing time: 30 min, centrifugation rate: 2500 rpm, centrifugation time: 5 min).

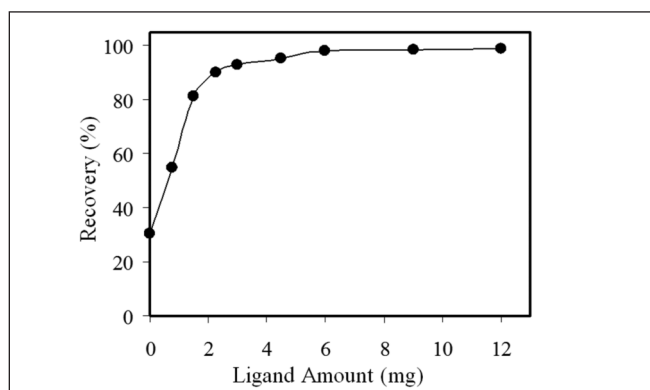


Fig. 3. Effect of BODAH amount on the recovery of Au(III) ions (N: 3, pH: 3.5, sample volume: 50 mL).

conducted in the standing time range of 0–120 minutes, centrifugation rate range of 1000–3500 rpm, and centrifugation time range of 5–30 minutes. It was observed that for the formation of a quality precipitate, the standing time, centrifugation rate and time were optimum at 30 minutes, 2500 rpm, and 5 minutes, respectively, at a constant pH and a fixed quantity of the coprecipitating agent (Table II).

Because natural water samples contain alkali, alkaline earth, and some transition metal ion salts at relatively high concentrations, the effects of these matrix constituents on the quantitative recoveries of Au(III) ions were investigated. Therefore, different amounts of each of the foreign ions, which are the major components of sea and stream water, were added to the model solutions containing 4.0 µg

of Au(III) ions under the optimum conditions. As seen from Table III, the existence of several anions and cations, including the transition metal ions, did not have any significant interfering effects on the recovery of the Au(III) ions under the selected conditions. Consequently it can be concluded that the recommended CEFC procedure can be applied to samples consisting of various foreign ions at allowable levels.

Analytical Performance of the Method

The limit of detection (LOD), defined as the concentration that gives a signal equivalent to three times the standard deviation of

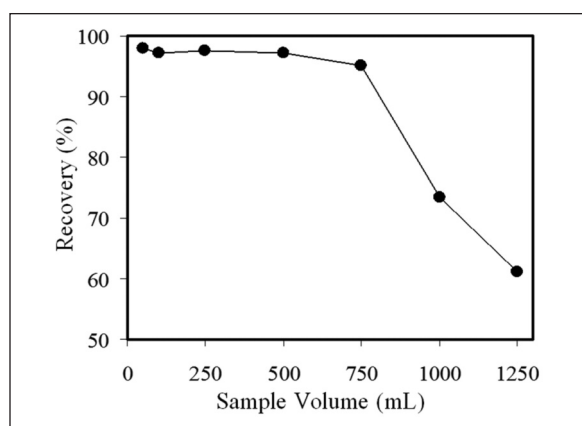


Fig. 4. Effect of sample volumes on the recovery of Au(III) ions (N: 3, pH: 3.5).

TABLE II
Effect of Standing Time, Centrifugation Rate and Time on the Recovery of Au(III) Ions (N: 3, pH: 3.5, sample volume: 50 mL, quantity of BODAH: 6.0 mg)

	Au(III) (Rec. %)	
Standing time (minutes)	0	82.5 ± 2.1
	5	92.0 ± 4.4
	10	94.3 ± 2.0
	20	93.7 ± 3.6
	30	96.6 ± 1.6
	60	96.3 ± 1.6
Centrifugation rate (rpm)	1000	91.4 ± 2.0
	2000	93.2 ± 1.1
	2500	97.7 ± 1.8
	3000	98.6 ± 2.5
	3500	100.5 ± 3.3
Centrifugation time (minute)	5	101.1 ± 3.0
	10	102.3 ± 2.3
	20	96.3 ± 3.8
	30	97.5 ± 2.5

TABLE III
Influences of Some Foreign Ions on Recovery of Au(III) (N: 3, pH: 3.5, sample volume: 50 mL, quantity of BODAH: 6.0 mg, standing time: 30 min, centrifugation rate: 2500 rpm, centrifugation time: 5 min)

Ions	Added as	Conc. (mg L ⁻¹)	Au(III) Rec.(%)
Na ⁺	NaCl	10000	99.1 ± 0.9
K ⁺	KCl	1000	92.3 ± 1.8
Ca ²⁺	CaCl ₂	1000	95.8 ± 4.9
Mg ²⁺	Mg(NO ₃) ₂	1000	92.8 ± 0.8
NO ₃ ⁻	NaNO ₃	5000	91.8 ± 4.7
CO ₃ ²⁻	Na ₂ CO ₃	1000	93.1 ± 2.7
SO ₄ ²⁻	Na ₂ SO ₄	1000	98.3 ± 2.4
PO ₄ ³⁻	Na ₃ PO ₄	1000	98.6 ± 2.0
F ⁻	NaF	250	90.8 ± 4.3
CH ₃ COO ⁻	NaCH ₃ COO	250	92.5 ± 4.3
Hg(II), Sb(III), Se(II), Mo(VI), As(III), Bi(III), Cr(III), Cd(II), Pb(II), Sn(II), Co(II), Cu(II), Mn(II), Zn(II), Al(III), Ni(II)		* **	90.9 ± 4.8
Mixture ^a			92.0 ± 1.1

* Sb(III); Sb₂O₃, Se(II); SeO₂, Mo(VI); (NH₄)₆Mo₇O₂₄·4H₂O, As(III); As₂O₃, Bi(III); BiO(NO₃), Sn(II); SnCl₂ and other ions added as their nitrate salts.

**2 mg L⁻¹ Hg(II), Sb(III), Se(II), Mo(VI), As(III), Bi(III); 20 mg L⁻¹ Cr(III), Cd(II), Pb(II), Sn(II), Co(II), Cu(II), Mn(II), Zn(II), Al(III), Ni(II).

^a 10,750 mg L⁻¹ Na⁺; 16,113 mg L⁻¹ Cl⁻; 1868 mg L⁻¹ NO₃⁻; 250 mg L⁻¹ K⁺, Ca²⁺, Mg²⁺, CO₃²⁻, SO₄²⁻, PO₄³⁻, F⁻, and CH₃COO⁻; 2 mg L⁻¹ Hg(II), Sb(III), Se(II), Mo(VI), As(III), Bi(III), Cr(III), Cd(II), Pb(II), Sn(II), Co(II), Cu(II), Mn(II), Zn(II), Al(III), and Ni(II).

10 replicate measurements of the blank samples, for Au(III) ions was found to be $0.36 \mu\text{g L}^{-1}$ when the sample volume was 750 mL and the final volume 2.0 mL. In order to evaluate the precision of the developed CEFC method, the procedure ($4.0 \mu\text{g}$ of Au(III) ions in 50 mL of aqueous solution) was repeated 10 times under the optimum conditions, and the relative standard deviation (RSD) was found to be 5.1%.

Method Validation and Application to Real Samples

In order to demonstrate the accuracy of the proposed separation and preconcentration method,

spike/recovery tests were applied to solid and liquid samples under the optimum conditions: anodic slime (HES/Kayseri, Turkey), gold ore (Ordu/Akoluk), soil (Kanuni Campus, Karadeniz Technical University, Trabzon, Turkey), seawater (Blacksea, Trabzon), and stream water (Sana, Trabzon). Different amounts of Au(III) ions were added to the digested solid (Table IV) and liquid samples (Table V). Then the recommended procedure, as described in the "Model Studies for Coprecipitation" section, was applied to these solutions. The results revealed good congruence between the added and measured analyte amounts. As seen from

Tables IV and V, the results revealed good agreement between the added and measured analyte amounts. The certified reference material CRM-SA-C Sandy Soil C was also used for method validation, and good agreement was found between the obtained and certified values (Table VI).

The present CEFC method was finally applied to real solid (anodic slime, gold ore, and soil) and liquid samples (seawater and stream water). The results obtained from the real samples are summarized in Table VII.

TABLE IV
Spiked Recoveries of Au(III) Ions From Solid Samples (N: 3, pH: 3.5, final volume: 2.0 mL)

Element	Added (μg)	Anodic Slime		Gold Ore		Soil	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Au(III)	0	23.83 ± 0.89	-	2.22 ± 0.08	-	0.64 ± 0.11	-
	5.0	28.56 ± 1.41	94.6	6.86 ± 0.45	92.8	5.16 ± 0.91	90.4
	10.0	33.14 ± 1.58	93.1	11.67 ± 0.76	94.5	10.11 ± 0.94	94.7

TABLE V
Spiked Recoveries of Au(III) Ions From Water Samples (N: 3, pH: 3.5, sample volume: 50 mL, final volume: 2.0 mL)

Element	Added (μg)	Seawater		Stream Water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Au(III)	0	BDL*	-	BDL	-
	5.0	4.78 ± 0.13	95.6	4.80 ± 0.11	96.0
	10.0	9.40 ± 0.42	94.0	9.48 ± 0.38	94.8

* Below detection limit.

TABLE VI
Application of Present Method to CRM-SA-C Sandy Soil C (N:3; pH: 3.5; quantity of Sandy Soil C: 0.250 g; final volume: 2.0 mL)

Element	CRM-SA-C Sandy Soil C Certified Value ($\mu\text{g g}^{-1}$)	Found Value ($\mu\text{g g}^{-1}$)
Au(III)	25.5 ± 0.1	22.1 ± 1.4

TABLE VII
Au(III) Ion Levels in Real Solid/Liquid Samples By Using the Presented Coprecipitation Procedure (N: 3, sample volumes: 750 mL, sample quantities: 0.100 g of anodic sludge and gold ore, 0.750 g of soil, final volume: 2.0 mL)

Element	Liquid Samples ($\mu\text{g L}^{-1}$)		Solid Samples ($\mu\text{g g}^{-1}$)		
	Seawater	Stream Water	Anodic Slime	Gold Ore	Soil
Au(III)	6.72 ± 0.49	8.83 ± 0.31	238.30 ± 3.89	22.20 ± 0.31	0.85 ± 0.04

CONCLUSION

An accurate and precise preconcentration/matrix separation approach to assist in the measurement of low levels of Au(III) ions in industrial and environmental solid and liquid samples based on the carrier element-free coprecipitation (CEFC) method was investigated. BODAH, an organic coprecipitating agent (N-benzyl-2-([3-methyl-4-(2-morpholine-4-ylethyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazole-1-yl] acetyl)hydrazinecarboxamide), allows effective and selective separation and preconcentration of Au(III) ions by collecting the analyte ion on itself without using a carrier element. Contamination risk for the analyte ions from a carrier element was therefore eliminated. The proposed CEFC method is also environmentally friendly since this method enables to use less chemicals. The method was optimized to give quantitative recoveries (>95%) of the Au(III) ions and was successfully applied for the determination of Au(III) ions in environmental solid and liquid samples with a low detection limit and high accuracy and precision.

Received June 24, 2013.

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