

Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations

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Abstract

An enrichment-separation procedure based on the coprecipitation of gold(III), palladium(II) and lead(II) ions with nickel(II)-5-methyl-4-(2-thiazolylazo) resorcinol complex has been developed. The analytical parameters including pH, amounts of 5-methyl-4-(2-thiazolylazo) resorcinol, sample volume, etc. was investigated for quantitative recoveries of Au(III), Pd(II) and Pb(II). Interference due to various cations and anions has also been investigated. The detection limits for analyte ions by 3σ were $2.6 \mu\text{g L}^{-1}$ for lead, $1.5 \mu\text{g L}^{-1}$ for gold, $2.1 \mu\text{g L}^{-1}$ for palladium. The accuracy of the method was evaluated by the analysis of certified reference materials (NIST SRM 2711 Montana soil, GBW 07309 Stream sediment). The proposed procedure was successfully applied to environmental samples for the determinations of analytes.
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1. Introduction

The monitoring of the levels of heavy metal ions in environmental samples is an important part of analytical chemistry due to their positive and/or negative influences on the human body [1–3]. Some metals including manganese, iron, copper, zinc and cobalt are essential micronutrients and have a variety of biochemical functions in all living organisms. While these elements are essential, they can be toxic when taken in excess [2–4]. However, some metals like lead and cadmium are non-essential metals as they are toxic, even in traces [3–5].

The determination of trace heavy metal ions in environmental samples by flame atomic absorption spectrometry (FAAS) is directly difficult even with background correction and chemical modification; not only because of the presence of many trace metals at concentrations near or below detection limit, but also because the analyzed sample matrix may cause serious interference [6–10]. In order to solve these problems, preconcentration-separation procedures have been continuously done by the several researchers [11–14]. Various method of

preconcentration-separation of analytes prior to the determination with FAAS or GFAAS based on solvent extraction, ion exchange, membrane filtration, cloud point extraction, and solid phase extraction have been developed [15–21].

Coprecipitation is a preconcentration technique of rapidly growing importance in trace heavy metal determination with flame or graphite furnace atomic absorption spectrometry. There has been sustained interest in the application of coprecipitation to various contaminants in complex matrix environmental samples. It is one of the most effective multi-element preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor among the preconcentration/separation methods [22–29]. Various carrier element-organic ligand combinations have been used for the coprecipitation of traces heavy metal ions in environmental samples including natural water and food samples [25–32]. According to our literature survey, no coprecipitation study is performed by using the combination of nickel(II) and 5-methyl-4-(2-thiazolylazo) resorcinol.

In the presented work, simple and rapid coprecipitation procedure by using nickel(II)-5-methyl-4-(2-thiazolylazo) resorcinol precipitate has been proposed for gold(III), palladium(II) and lead(II) in environmental samples prior to their flame atomic absorption spectrometric determinations.

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2. Experimental

2.1. Instrument

Perkin–Elmer Model 3110 and Perkin Elmer AAnalyst 700 atomic absorption spectrometer were used in the studies. All measurements were carried out in an air/acetylene flame. Ten centimeters long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements were set as recommended by the manufacturer. Hettich Rotofix 32 model, Nuve NF 800 model and Mistral 2000 model centrifuges were used to centrifuge of solutions. The water was purified in a Human model RO 180, resulting water with a conductivity of $1 \mu\text{S cm}^{-1}$.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300°C) was used. Digestion conditions for microwave system for real samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, ventilation: 8 min.

2.2. Reagents and solutions

All the reagents used were of analytical reagent grade. Deionized double distilled water was used throughout. Laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution and then rinsed with deionized double distilled water. Hundred milliliters of 5-methyl-4-(2-thiazolylazo) resorcinol (MTR) (CAS number: 37422-56-3) solution (0.1%, w/v) was daily prepared in ethanol.

A stock solution of nickel(II) (1000 mg L^{-1}) was prepared by $\text{Ni}(\text{NO}_3)_2$ (E-Merck, Germany) in deionized doubly distilled water. It was prepared daily. Stock standard solutions of analytes, 1000 mg L^{-1} , was prepared by dissolving appropriate amount of nitrate salts of analytes in 1% nitric acid. Stock metal ion solutions were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 mol L^{-1} HNO_3 by dilution from stock solutions.

Phosphate buffer solution ($\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and phosphoric acid solutions for pH 2. Acetate buffer solutions ($\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate solutions for pH 4. Phosphate buffer solutions ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and 1 mol L^{-1} sodium hydrogen phosphate for pH 5 and 6. Ammonium buffer solutions were prepared by mixing of appropriate amounts of 1 mol L^{-1} ammonia and 1 mol L^{-1} ammonium chloride solutions for pH 8.

2.3. Coprecipitation procedure

The nickel-5-methyl-4-(2-thiazolylazo) resorcinol coprecipitation method was tested with model solutions prior to its

application to real samples. Twenty milliliters portion of an aqueous solution containing $20 \mu\text{g}$ of Au(III), Pd(II) and Pb(II) was placed in a centrifuge tube. The pH of solution was adjusted with an appropriate buffer solution. Then 1.0 mL of 1000 mg L^{-1} of nickel(II) as a carrier element was added to this solution. The required volume of 5-methyl-4-(2-thiazolylazo) resorcinol solution was poured into the tube. After 10 min, the solution was centrifuged at 2500 rpm for 20 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1.0 mL of concentrated HNO_3 . Then the final volume was completed to 5.0 or 10.0 mL with deionized double distilled water. The number of replicates for the test workings was three. The analytes were determined by flame atomic absorption spectrometry.

2.4. Analysis of real samples

NIST SRM 2711 Montana soil and GBW 07309 Stream sediment (250 mg), soil, sediment and street dust (1.0 g) were digested with 6 mL of HCl (37%), 2 mL of HNO_3 (65%) in microwave digestion system and diluted to 50 mL with deionized water. Lichen (*Protoparmeliopsis muralis*) samples (1.0 g) were digested with 6 mL of concentrated HNO_3 (65%) and 2 mL of H_2O_2 (30%) in microwave system and diluted to 50 mL with deionized water [33–35]. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry.

Natural water samples analyzed were filtered through Millipore cellulose membrane filter ($0.45 \mu\text{m}$ pore size). The pH of the samples was adjusted to 4.0 with buffer solution. Then the preconcentration procedure given above was applied to the final solutions. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Effects of pH

The influences of pH of the sample solution on the recoveries of gold(III), palladium(II) and lead(II) ions were investigated in the pH range of 2.0–8.0. The results for this study were given in Fig. 1. Gold(III) and palladium(II) were recovered quantitatively at the pH range of 2.0–6.0. The quantitative recoveries for lead(II) in the presented system was obtained at pH range of 4.0–6.0. For all subsequent works, pH 4.0 was selected as working pH for each analyte ions.

3.2. Influences of ligand amount

The effects of amounts of 5-methyl-4-(2-thiazolylazo) resorcinol on the recoveries of analyte ions were examined. The results are depicted in Fig. 2. When the experiments were performed without 5-methyl-4-(2-thiazolylazo) resorcinol at pH 4.0, the recoveries of the analyte ions were not quantitative. The recoveries of analytes ions increased with increasing amounts of

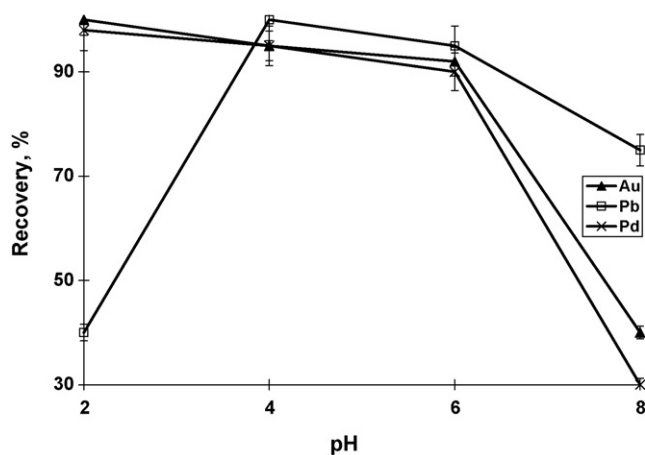


Fig. 1. Influences of pH on the recoveries of analyte ions ($n=3$).

5-methyl-4-(2-thiazolylazo) resorcinol. Quantitative recoveries were obtained for all three analytes after 1.0 mL of 0.5% (w/v) 5-methyl-4-(2-thiazolylazo) resorcinol. All subsequent works were carried out with 1.0 mL of 0.5% (w/v) 5-methyl-4-(2-thiazolylazo) resorcinol.

3.3. Amount of nickel as carrier element

The influences of amounts of nickel(II) as carrier element on the recoveries of analyte ions were also investigated. Without nickel, the recoveries for analyte ions were below 55% on the presented coprecipitation system. Quantitative recovery values (>95%) for the analyte ions were obtained for all analyte ions in 1.0–3.0 mg of nickel(II) as carrier element. All further works were performed with 1 mg (1 mL of 1000 mg L⁻¹) of nickel(II) ions as carrier element.

3.4. Influences of sample volume

To obtain high preconcentration factor, volume of the sample solution is an important parameter. Because of this point, the influences of the sample volume on the coprecipitation

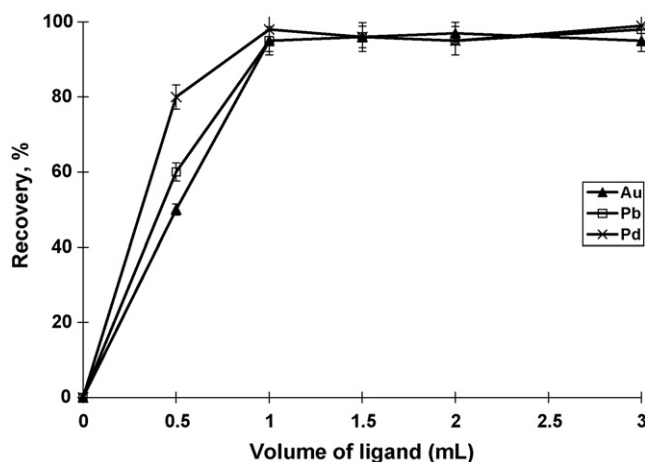


Fig. 2. Influences of ligand amount on the recoveries of analytes ($n=3$).

itation efficiencies of the analytes were examined. Analyte ions were quantitatively recovered in the sample volume range of 10–50 mL. The precipitate of nickel(II)-5-methyl-4-(2-thiazolylazo) resorcinol that was including analytes was successfully dissolved 1.0 mL of concentrated nitric acid. The final volume was completed to 2.0, 5.0 or 10.0 mL by deionized double distilled water. The analytes were quantitatively recovered in these studies. The preconcentration factor is calculated by the ratio of the highest sample volume for each analytes and the lowest final volume (2 mL). The preconcentration factor for analytes was 25.

3.5. Interference studies

In order to assess the possible analytical applications, the effect of some foreign ions in various real samples was examined with the optimized conditions at above. For these studies, a fixed amount of analytes was taken with different amounts of foreign ions and recommended procedure given in Section 2 was followed. The recoveries of analyte ions were generally higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of analytes by the combination of the coprecipitation method presented and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 1. As it is seen, large numbers of metal ions used have no considerable effect on the determination of analyte ions.

3.6. Addition/recovery tests

In order to estimate the accuracy of the presented coprecipitation procedure, different amounts of the investigated metal ions were spiked in a tap water from Tokat, Turkey, spring water from Tokat, Turkey and a seawater samples from Blacksea. The

Table 1
Influences of some foreign ions on the recoveries of analytes ($n=3$)

Ion	Added as	Concentration (mg L ⁻¹)	Pb	Au	Pd
Na ⁺	NaCl	25000	95 ± 2	96 ± 3	95 ± 3
K ⁺	KCl	3000	96 ± 3	97 ± 4	98 ± 4
Ca ²⁺	CaCl ₂	3000	95 ± 3	96 ± 3	97 ± 3
Mg ²⁺	MgCl ₂	2000	96 ± 4	97 ± 3	95 ± 3
Cl ⁻	NaCl	25000	95 ± 3	96 ± 2	96 ± 4
F ⁻	NaF	1000	96 ± 4	98 ± 1	99 ± 2
NO ₃ ⁻	KNO ₃	2000	97 ± 2	97 ± 3	96 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	2000	96 ± 3	95 ± 2	97 ± 2
PO ₄ ³⁻	Na ₃ PO ₄	1000	96 ± 4	98 ± 2	95 ± 2
Al ³⁺	Al ₂ (SO ₄) ₃	50	98 ± 2	97 ± 2	97 ± 2
Ag ⁺	Ag NO ₃	50	96 ± 2	95 ± 3	95 ± 3
Cu ²⁺	CuSO ₄	50	95 ± 2	97 ± 3	96 ± 2
Mn ²⁺	MnSO ₄	50	97 ± 2	96 ± 3	95 ± 3
Zn ²⁺	ZnSO ₄	50	95 ± 3	97 ± 2	96 ± 3
Fe ³⁺	Fe ₂ (SO ₄) ₃	50	95 ± 1	95 ± 3	96 ± 3
Cr ³⁺	Cr(NO ₃) ₃	50	96 ± 2	95 ± 1	97 ± 2
Cd ²⁺	Cd(NO ₃) ₂	50	98 ± 4	96 ± 3	99 ± 3
Ni ²⁺	NiSO ₄	50	95 ± 3	97 ± 2	96 ± 4
Co ²⁺	CoSO ₄	50	98 ± 3	95 ± 3	96 ± 3

Table 2
The results for tests of addition/recovery for Pb, Au and Pd

Element	Added (μg)	Tap water		Sea water		Spring water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb	0	ND	–	ND	–	ND	–
	10	9.9 ± 0.3^a	99	9.7 ± 0.5	97	9.6 ± 0.4	96
	20	19.5 ± 0.9	98	19.2 ± 0.8	96	19.4 ± 0.7	97
	40	38.7 ± 1.2	97	38.4 ± 1.5	96	39.1 ± 1.3	98
Au	0	ND	–	ND	–	ND	–
	10	9.7 ± 0.5	97	9.5 ± 0.4	95	9.7 ± 0.6	97
	20	19.7 ± 0.8	99	19.5 ± 0.9	98	19.3 ± 0.9	97
	40	39.3 ± 0.9	98	38.5 ± 1.6	96	38.1 ± 1.5	95
Pd	0	ND	–	ND	–	ND	–
	10	9.8 ± 0.4	98	9.8 ± 0.6	98	9.9 ± 0.5	99
	20	19.8 ± 0.7	99	19.4 ± 0.7	97	19.3 ± 1.1	97
	40	39.4 ± 1.1	99	38.6 ± 0.9	97	38.2 ± 1.8	96

^a Standard deviation ($n=4$), N.D.: not detected.

Table 3
The results for reference standard materials ($n=5$)

Element	NIST SRM 2711 Montana soil ($\mu\text{g g}^{-1}$)		GBW 07309 Stream sediment ($\mu\text{g g}^{-1}$)	
	Certified value	Our value	Certified value	Our value
Pb	1162	1125 ± 50	23	22.1 ± 0.9
Au	(0.03) ^a	BDL	(0.0013)	BDL
Pd	–	BDL	–	BDL

BDL: below the detection limit.

^a The value in the parenthesis is not certified.

resulting solutions were submitted to the presented procedure given in Section 2. The results were given in Table 2. The recovery values for analyte ions were generally higher than 95%. A good agreement was obtained between the added and measured analyte amounts. It shows that the presented method can be applied for coprecipitation of analyte ions in the real samples which have high salt content.

3.7. Analytical performance

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions were below 10%. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n=10$) of the reagent blank, for Pb(II), Pd(II) and Au(III) were 2.6, 1.5 and $2.1 \mu\text{g L}^{-1}$, respectively.

3.8. Application to real samples

The presented coprecipitation procedure was evaluated using the certified reference materials (NIST SRM 2711 Montana soil and GBW 07309 Stream sediment) for analyte ions. The results were given in Table 3. The obtained results were in good agreement with the certified values.

The proposed coprecipitation procedure has been also applied to different natural waters for the enrichment and separation of analyte ions. The results are given in Table 4. The method

Table 4
Pb, Au and Pd in some liquid samples^a

Samples	Concentration ($\mu\text{g L}^{-1}$)		
	Pb	Au	Pd
Tap water	6.5 ± 0.3^b	BDL	BDL
Sea water	4.8 ± 0.2	BDL	BDL
Spring water	8.7 ± 0.5	BDL	BDL
River water	7.3 ± 0.6	BDL	BDL

^a Final volume: 2 mL, $n=4$.

^b Mean expressed as 95% tolerance limit, BDL: below the detection limit.

has been combined with the microwave assisted digested samples. The results are given in Table 5. The results have been calculated on the assumption of 100% recovery of analyte ions.

Table 5
Concentration of analyte ions in microwave digested solid samples^a

Samples	Concentration ($\mu\text{g g}^{-1}$)		
	Pb	Au	Pd
Soil	7.5 ± 0.6^b	BDL	BDL
Sediment	12.8 ± 0.9	BDL	BDL
Street dust	145.7 ± 13.5	BDL	0.50 ± 0.04
Lichen (<i>Protopermaliopsis muralis</i>)	16.5 ± 1.2	BDL	0.75 ± 0.05

^a $n=5$, final volume: 2 mL.

^b Mean expressed as 95% tolerance limit, BDL: Below the detection limit.

Table 6
Optimum preconcentration conditions in experimental studies

Parameters	Optimum conditions
pH	4
Ligand amount	1.0 mL of 0.5% (w/v)
Amount of nickel	1 mg
Sample volume (mL)	50
Enrichment factor	25

4. Conclusion

The coprecipitation with 5-methyl-4-(2-thiazolylazo) resorcinol-nickel(II) system offers a useful multielement preconcentration technique in environmental samples. The procedure has been successfully applied to analyte ions with acceptable accuracy and precision. The time required for the coprecipitation and determination was about 30 min. Under conditions given in Table 6, the determination of analyte ions yields quantitative recoveries. The effect of matrix can be overcome by the method, and the results are satisfying. The method proposed here is rapid and has good reproducibility. The usefulness of the method is shown by the control analyses of standard reference materials. The detection limits of analytes are superior to those of preconcentration techniques for analyses [27–29,36–41]. The good features of the proposed method showed that it is a convenient and low cost one. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of analytes.

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