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Short Report

Development of a New Solid Phase Extraction Procedure for Selective Separation and Enrichment of Au(III) Ions in Environmental Samples

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Um procedimento de extração em fase sólida (SPE) altamente sensível, seletivo e de baixo custo foi desenvolvido para separação e enriquecimento de íons Au(III) em amostras ambientais previamente a sua detecção por espectrometria de absorção atômica com chama (FAAS). O complexo Au(III)-2-piridina-5-(4-toluil)-1,3,4-oxadiazol (PYTOX) foi quantitativamente adsorvido em resina Amberlite XAD-4 na condição de HNO_3 0,5 mol L^{-1} e a eluição foi realizada com 7,5 mL de HCl 1,0 mol L^{-1} em acetona. Alguns parâmetros analíticos afetam as recuperações de íons Au(III), tais como concentração de HNO_3 da solução da amostra, quantidade de PYTOX, tipo, concentração e volume do eluente, volume de amostra e concomitantes. Sob condições experimentais ideais, o limite de detecção para Au(III) foi 1,03 µg L^{-1}, com fator de pré-concentração de 50 e desvio padrão relativo (RSD) de 3,7%. A determinação de íons Au(III) em resíduo anódico, minério de ouro, solo e águas de mar e de rio foi efetuada após verificação da exatidão do método por testes de adição e recuperação.

A highly sensitive, selective and low cost solid phase extraction (SPE) procedure was developed for separation and enrichment of Au(III) ions in environmental samples prior to its flame atomic absorption spectrometric detection. Au(III)-2-pyridin-5-(4-tolyl)-1,3,4-oxadiazole (PYTOX) complex was adsorbed quantitatively on Amberlite XAD-4 resin in 0.5 mol L^{-1} HNO_3 condition and the elution was carried out with 7.5 mL of 1.0 mol L^{-1} HCl in acetone. Some analytical parameters, affect the recoveries of Au(III) ions, such as HNO_3 concentration of sample solution, amount of PYTOX, type, concentration and volume of eluent, sample volume and concomitants were examined. Adopting optimized experimental conditions, the limit of detection for Au(III) ions was 1.03 µg L^{-1} with preconcentration factor of 50 and a relative standard deviation (RSD) of 3.7%. The determination of Au(III) ions in anodic slime, gold ore, soil and sea and stream waters was performed after checking the accuracy of the method by addition-recovery tests.

Keywords: separation, preconcentration, Amberlite XAD-4, gold, anodic slime

Introduction

Gold, one of the precious metals, is present on Earth in very low levels. Its products are widely used in several industrial applications including medicine, electronics, petrochemical industry and nuclear power industry.[1] Its concentration is about 4.0 ng g^{-1} in basic rocks, 5.0 ng g^{-1} in ultrabasic rocks, 4.5 ng g^{-1} granitoide rocks and 1.0 ng g^{-1} in soils. Apart from these, Au(III) levels are 0.05 and 0.2 µg L^{-1} in sea and river water, respectively.[2-4]

The determination of Au(III) ions is generally difficult in environmental, geological and metallurgical materials because of high interfering effects of matrix components and also lower levels of Au(III) than the limit

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of detection of the instrumental methods. Consequently, to enhance the sensitivity and accuracy of the analyses and to eliminate matrix effects, separation and preconcentration techniques are usually necessary.[5,6]

Various techniques such as coprecipitation,[7,8] solid phase extraction (SPE),[2,9,10] cloud point extraction,[11] liquid-liquid extraction[12] and electrodeposition[13] have been used for separation and enrichment of Au(III) ions. Solid phase extraction has a wide range of applications in comparison with other preconcentration methods because of its several advantages including simple operation and easy automation, obtaining high enrichment factor, rapid phase separation, reusability of adsorbent, environmentally friendly and inexpensive due to low consumption of chemical reagents.[14,15]

In the presented method, a selective SPE procedure has been proposed for Au(III) ions by using Amberlite XAD-4 adsorption resin and 2-pyridin-5-(4-tolyl)-1,3,4-oxadiazole (PYTOX) as a complexing reagent prior to its flame atomic absorption spectrometric (FAAS) determinations. At the beginning of the study, the selectivity of PYTOX towards the quantitative recovery values of several metal ions, such as Au(III), Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), Fe(III), Ni(II), Zn(II), Pd(II) and Pt(IV), was tested. For optimization of the developed procedure, experimental conditions were examined in detail. After checking the accuracy of the procedure, it was applied to anodic slime, gold ore, soil and sea and stream waters to determine their Au(III) concentrations.

Experimental

Apparatus

A Perkin Elmer AAnalyst 400 flame atomic absorption spectrometer equipped with deuterium lamp background corrector was used for determination of Au(III) and also other metal ion levels. The instrumental settings of the spectrometer for Au(III) ion detection were as follows: wavelength at 242.80 nm, spectral resolution of 2.7 nm, lamp applied current at 10 mA, acetylene flow rate of 2.5 L min^{-1} and air flow rate of 10.0 L min^{-1}. The pH adjustments were carried out using a Hanna pH-211 (Hanna Instruments, Romania) digital pH meter with a glass electrode. A closed vessel microwave system (Milestone Ethos D) was used for digestion of solid samples.

Reagents and solutions

All chemical reagents were obtained from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). 1000 mg L^{-1} stock solutions of metal ions were diluted to obtain standard and working solutions. Distilled/deionized water (Sartorius Milli-Q system) was used in all the experiments. For adjustment of the pH values of aqueous solutions, 0.1 mol L^{-1} HNO_3 and NaOH solutions were used. PYTOX was synthesized[16] according to the literature and 0.2% m v^{-1} PYTOX solution was prepared in ethanol.

Column preparation

The Amberlite XAD-4 resin was washed according to the literature.[15] It was dried at 105 ºC in an oven. A mass of 250 mg washed resin was slurred in water and poured into the column (10.0 cm length and 1.0 cm diameter) with a porous disk and stopcock. After each use, the resin was conditioned with 1.0 mol L^{-1} HNO_3 in acetone, and then stored in water for further application.

Analytical procedure

Volumes of 25 mL of sample solutions containing 20 µg of Au(III) were prepared in 0.5 mol L^{-1} HNO_3, and then 0.5 mL (0.2% m v^{-1}) of PYTOX solution was added to them. After standing for 15 min, the resulting solution was passed through the column with a flow rate of 20 mL min^{-1}. The retained metal ions on the resin were eluted with 7.5 mL of 1.0 mol L^{-1} HCl solution in acetone. The eluent was evaporated to near dryness on a hot plate and volume was made up to 5.0 mL with distilled water. Finally, solutions were analyzed for their Au(III) levels by FAAS.

Sample preparation

The stream water (Şana River, Trabzon, Turkey) and sea water (Blacksea, Trabzon, Turkey) samples were collected in prewashed polyethylene bottles. First of all, the water samples were filtered through a cellulose nitrate membrane and after acidified with 1% v v^{-1} HNO_3 solution, they were stored at 4 °C in a refrigerator. When the water samples were used in the experiments, appropriate amount of PYTOX was added and the developed procedure was applied.

Anodic slime, soil and gold ore samples were microwave-assisted acid digested. Masses of 0.100 g of gold ore and anodic slime and 0.750 g of soil samples were weighed into PTFE vessels, separately. Volumes of 1.5 mL of HNO_3, 4.5 mL of HCl, 2 mL of H_2O_2 and 2 mL HF were added into the vessels. The digestion conditions were set according to the literature.[17] The volume of the digests was made up to 50.0 mL with distilled water and the developed procedure was applied.

Results and Discussion

Parameter optimization

The experimental parameters which affect the quantitative recoveries of Au(III) were studied in detail and optimized, before applying the procedure to environmental samples. First of all, the influence of the HNO_3 concentration on recoveries of Au(III) and also other metal ions including Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), Fe(III), Ni(II), Zn(II), Pd(II) and Pt(IV) was studied in HNO_3 concentration range of 0.01-3.0 mol L^{-1}. Although recoveries of Au(III) ions were quantitative in the 0.25-3.0 mol L^{-1} HNO_3 concentration range, the recovery values were lower than 5% for other metal ions. The effect of HNO_3 concentration on the recoveries of the Au(III) ions is shown in Figure 1. Au(III) were quantitatively separated from other metal ions in the 0.25-3.0 mol L^{-1} HNO_3 concentration range. Thus, for selective separation and preconcentration of Au(III) ions, 0.5 mol L^{-1} HNO_3 medium was recommended.

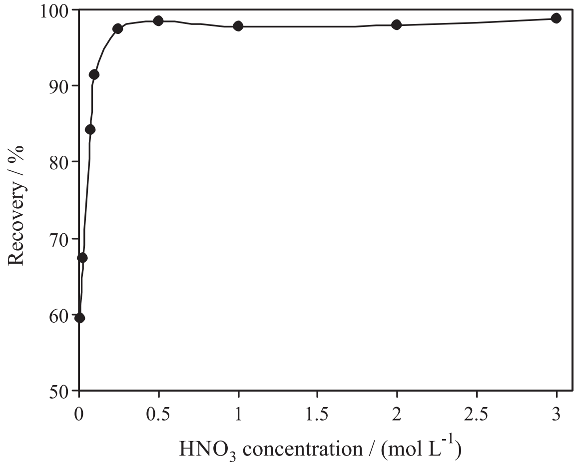

Figure 1. Relation between HNO_3 concentration and recovery values (*N*:3, PYTOX amount: 1.0 mg, eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone, and sample volume: 50 mL).

Effects of PYTOX amount on recoveries of Au(III) were examined in the PYTOX amount range of 0-4.0 mg (0-2.0 mL, 0.2% m v^{-1}). Au(III) ion recoveries were quantitative in the PYTOX amount range of 1.0-4.0 mg (Figure 2). Above 2.0 mg of PYTOX amounts, recoveries were approximately constant. As a result, all further experiments were carried out by using 1.0 mg (0.5 mL of 0.2% m v^{-1} of PYTOX amount).

HNO_3 and HCl solutions, prepared in water, acetone and methanol at different concentrations, were tested as eluent solutions for desorption of Au(III) from Amberlite XAD-4 resin (Table 1). Quantitative recoveries (95%) for Au(III) were obtained when using 1.0 mol L^{-1} HCl solution in acetone as eluent. The effect of the eluent volume on the recovery of Au(III) was also studied in the eluent volume range of 2.5-10.0 mL. Quantitative recoveries were obtained with 7.5 mL of 1.0 mol L^{-1} HCl in acetone solution.

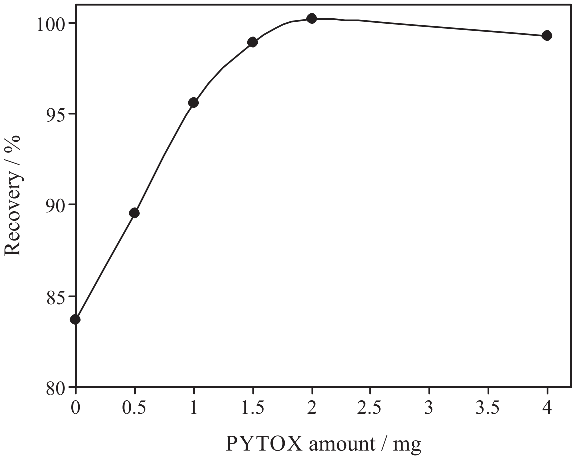

Figure 2. Effect of ligand quantities on the recovery of Au(III) (*N*:3, eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone, and sample volume: 50 mL).

Table 1. Effects of eluent type and concentration on the recovery of Au(III) (*N*:3, 0.5 mol L^{-1} HNO_3 conditions, PYTOX amount: 1.0 mg, and sample volume: 50 mL)

Eluent type and concentration	Recovery / %
1.0 mol L^{-1} HCl (in water)	9.1 ± 0.8
1.0 mol L^{-1} HNO_3 (in water)	6.0 ± 0.2
2.0 mol L^{-1} HCl (in water)	40.5 ± 1.6
2.0 mol L^{-1} HNO_3 (in water)	15.5 ± 0.1
1.0 mol L^{-1} HCl (in acetone)	98.6 ± 1.5
1.0 mol L^{-1} HNO_3 (in acetone)	23.5 ± 0.3
2.0 mol L^{-1} HCl (in acetone)	95.7 ± 1.3
2.0 mol L^{-1} HNO_3 (in acetone)	58.9 ± 1.4
1.0 mol L^{-1} HCl (in methanol)	88.4 ± 1.4
1.0 mol L^{-1} HNO_3 (in methanol)	7.7 ± 0.6

To evaluate the effect of the sample volume on the separation and preconcentration of Au(III), 50-1000 mL of sample solution containing 20 µg of Au(III) ions were processed. Recoveries of Au(III) were quantitative until 250 mL of sample volume (Figure 3). The preconcentration factor is calculated by the ratio of the highest sample volume and the lowest final volume, and it was found as 50 when the final volume was 5.0 mL.

Effects of matrix ions

The effects of some foreign ions on the retention of Au(III) on Amberlite XAD-4 resin were investigated by testing some common anions, cations and trace metal ions at different concentrations. Results are summarized in Table 2.

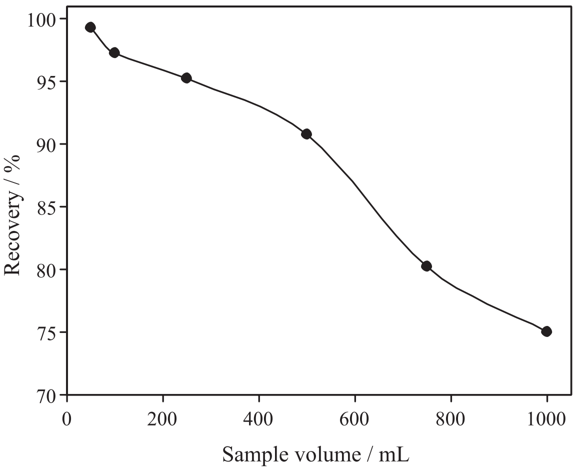

Figure 3. Effect of sample volume on the recovery of Au(III) (*N*:3, eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone).

Recoveries of Au(III) were generally higher than 90%. These results indicated that the developed procedure can be applied to samples containing high amount of salts and transition metal ions.

Table 2. Influence of matrix components on recoveries of Au(III) (*N*:3, 0.5 mol L^{-1} HNO_3 conditions, PYTOX amount: 1.0 mg, eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone, and sample volume: 50 mL)

Ion	Added as	Concentration / (mg L^{-1})	Recovery / %
Na^+	NaCl	5000	102.8 ± 3.2
K^+	KCl	1000	100.3 ± 3.1
Ca^{2+}	$CaCl_2$	1000	94.3 ± 1.1
Mg^{2+}	$Mg(NO_3)_2$	500	95.4 ± 2.3
NO_3^-	$NaNO_3$	5000	95.1 ± 3.4
CO_3^{2-}	Na_2CO_3	1000	91.2 ± 1.7
SO_4^{2-}	Na_2SO_4	1000	95.5 ± 4.4
PO_4^{3-}	Na_3PO_4	1000	91.6 ± 1.5
I^-	KI	100	95.3 ± 2.5
F^-	NaF	100	95.8 ± 4.0
CH_3COO^-	$NaCH_3COO$	250	94.3 ± 0.8
Cd(II), Ni(II), Al(III), Pb(II), Cr(III), V(V)	[a]	25	93.1 ± 0.6
Mixed[b]			94.3 ± 2.7

[a]V(V) added as V_2O_5, other ions added as their nitrate salts. [b]7428 mg L^{-1} Na^+, 8389 mg L^{-1} Cl^-, 6461 mg L^{-1} NO_3^-, 265 mg L^{-1} K^+, 250 mg L^{-1}, Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, 50 mg L^{-1} I^-, F^-, CH_3COO^-, 10 mg L^{-1} Cd(II), Ni(II), Al(III), Pb(II), Cr(III), V(V)

Adsorption capacity of the resin

To determine the adsorption capacity of the Amberlite XAD-4 resin, 50 mL of sample solutions containing different amounts of Au(III) in the range of 50-2000 µg were loaded to the column containing 250 mg of resin. The Langmuir isotherms were plotted in order to determine the resin capacity (Figure 4) , where q_e (mg g^{-1}) is the amount of Au(III) ions adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the equilibrium Au(III) ion concentration in aqueous solution. The maximum amount of Au(III) adsorbed onto 1.0 g of resin and the adsorption equilibrium constant were calculated as 2.7 and 0.137 L mol^{-1}, respectively.

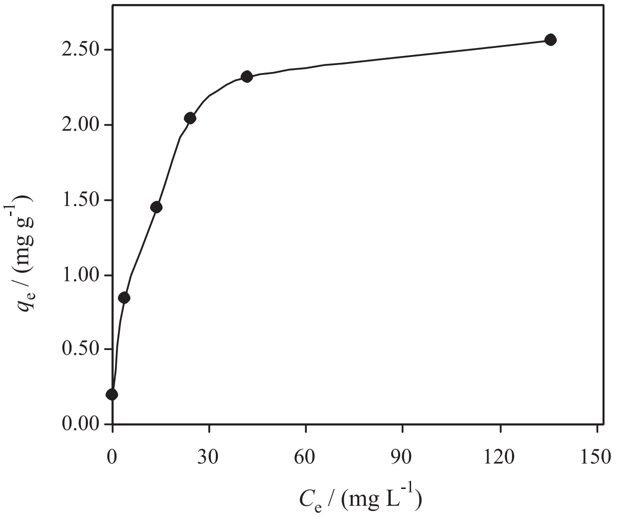

Figure 4. Langmuir adsorption isotherm for Au(III).

Analytical performance of the presented procedure

The limit of detection (LOD), defined as the concentration that gives a signal equivalent to three times the standard deviation of 10 replicate measurements of the blank samples, for Au(III) was found to be 1.03 µg L^{-1}. The precision of the procedure, expressed as relative standard deviation (RSD), was determined after analyzing a series of ten replicate solutions under the optimum conditions mentioned in the analytical procedure section, and it was found to be 3.7% for Au(III).

Accuracy test and application to real samples

In order to test the accuracy of the method, different amounts of Au(III) ions were added to liquid samples (sea and stream waters) (Table 3) and microwave-assisted

Table 3. Recoveries of Au(III) from water samples (*N*:3, 0.5 mol L^{-1} HNO_3 conditions, and sample volume: 50 mL)

Added / µg	Stream water		Sea water	
	Determined / µg	Recovered / %	Determined / µg	Recovered / %
0	< LOD[a]	–	< LOD[a]	–
10	9.45 ± 0.14	94.5	9.68 ± 0.25	96.8
20	19.23 ± 0.46	96.2	18.95 ± 0.57	94.8

[a]Below the limit of detection.

Table 4. Recoveries of Au(III) from solid samples (*N*:3, sample amount: 0.750 g of soil, 0.100 g of gold ore and anodic slime, and final volume: 5.0 mL)

Added / µg	Anodic slime		Gold Ore		Soil	
	Determined / µg	Recovered / %	Determined / µg	Recovered / %	Determined / µg	Recovered / %
0	21.15 ± 0.53	–	2.03 ± 0.12	–	< LOD[a]	–
10	30.93 ± 0.81	97.8	11.88 ± 0.25	98.5	9.25 ± 0.49	92.5
20	40.38 ± 1.24	96.2	21.08 ± 0.74	95.3	18.68 ± 0.60	93.4

[a] Below the limit of detection.

acid digested environmental solid samples (soil, anodic slime and gold ore) (Table 4). Then, the developed procedure was performed to determine Au(III). Good agreement was obtained between added and recovered values.

Lastly, the procedure was applied to soil, anodic slime, gold ore and sea and stream waters samples for the determination of trace amounts of Au(III) ions after being verified the accuracy of the method (Table 5).

Table 5. Au(III) contents in real samples after application of the presented SPE procedure (*N*:3, stream and sea water volume: 250 mL, amount of sample: 0.750 g of soil, 0.100 g of gold ore and anodic slime, and final volume: 5.0 mL)

Liquid sample / (µg L^{-1})		Solid sample / (µg g^{-1})		
Sea water	Stream water	Anodic slime	Gold ore	Soil
4.74 ± 0.12	9.64 ± 0.32	211.50 ± 5.30	20.30 ± 1.24	< LOD[a]

[a] Below the limit of detection.

Conclusion

The proposed Amberlite XAD-4/2-pyridin-5-(4-tolyl)-1,3,4-oxadiazole solid phase extraction system is a simple, highly selective and low cost method for separation and preconcentration of Au(III) in complex matrices. Most of the common ions present together with Au(III) do not interfere with the selectivity of the procedure. After optimizing the experimental parameters and checking the accuracy of the procedure, it was successfully applied to anodic slime, gold ore, soil and sea and stream waters to determine their Au(III) levels. The procedure was also compared with other reported SPE methods in terms of pH, preconcentration factor, limit of detection, relative standard deviation, adsorption capacity of the resin, type of the sample and determination technique.[2-4,6,18-23] First of all, the proposed method is less expensive with respect to the sorbent used[4,21,23] and the determination technique.[2,19,23] Contrary to many studies[3,19,21] given in Table 6, the suitability of the acidic medium for the selective separation, preconcentration and determination of Au(III) in complex matrices prevents the contamination risk that originates from the precipitation of different metal ions at high pH values. This also avoids the use of additional chemical reagent for adjusting the pH of the acid digested solid samples. On the other hand, although the adsorption capacity of the resin for Au(III) is lower in the proposed system than in other similar methods, it has high preconcentration factor,[18,19,20] low RSD[6] and relatively low LOD[6,18,20,22] values when compared with some of the other methods reported in Table 6.

Table 6. Comparison of the developed procedure with some recent studies based on SPE reported in literature

System	Analyte	pH	PF	LOD / (µg L^{-1}) for Au(III)	RSD / % for Au(III)	Adsorption capacity for Au(III) / (mg g^{-1})	Sample	Technique	Reference
Attapulgite modified with triocarbohydrazide	Au(III)	3.0	150	0.32	3.3	66.7	water	ICP-OES	2
Nanometer titanium dioxide immobilized on silica gel	Au(III)	8.0	50	0.21	1.8	3.56	geological and water samples	FAAS	3
Multiwalled carbon nanotubes	Au(III)	2.0	75	0.15	3.1	14.8	geological and water samples	FAAS	4
XAD-2000/ diethyldithiocarbamate	Au(III)	2.0 mol L^{-1} HNO$_3$ medium	200	16.6	< 6	12.3	soil and water samples	FAAS	6
Dowex M 4195	Au(III)	4.0	31	1.61	< 5	8.1	water, soil and sediment samples	FAAS	18
Mesoporous silica functionalized with 3-aminopropyl	Cu(II), Ag(I) and Au(III)	8.0-10.0	40	0.14	3.4	6.71 mmol g^{-1}	–	ET AAS	19

Table 6. continuation

System	Analyte	pH	PF	LOD / (µg L^{-1}) for Au(III)	RSD / % for Au(III)	Adsorption capacity for Au(III) / (mg g^{-1})	Sample	Technique	Reference
Amberlite XAD-2000	Au(III)	0.1 mol L^{-1} HCl medium	20	2.0	3.2		water and potassium salts	FAAS	20
Multiwalled carbon nanotubes modified with N,N'-bis(2-hydroxybenzylidene)-2,2'(aminophenylthio) ethane	Au(III) and Mn(II)	6.0	250	0.03	1.61	75	water	FAAS	21
Silica gel modified with benzoylthiourea	Au(III)	1.0 mol L^{-1} HCl medium	267	1.4	1.2	0.92 mmol g^{-1}	water	FAAS	22
Activated carbon modified with 2,6-diaminopyridine	Au(III), Pd(II) and Pt(IV)	1.0	75	0.16	< 3.0	202.7	ore and rock samples	ICP-OES	23
XAD-4/ Au(III)-2-pyridin-5-(4-tolyl)-1,3,4-oxadiazole	Au(III)	0.5 mol L^{-1} HNO_3 medium	50	1.03	3.7	2.7	water samples, soil, anodic slime and gold ore	FAAS	this work

PF: preconcentration factor; FAAS: flame atomic absorption spectrometry; ICP-OES: inductively coupled plasma optical emission spectrometry; ET AAS: electrothermal atomic absorption spectrometry.

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