Ionic Liquid-based Method for Microextraction/Enrichment of Gold from Real Samples and Determination by Flame Atomic Absorption Spectrometry

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INTRODUCTION

Gold occurs on earth at very low levels (1-3) with a concentration of about 4 ng g^{-1} in rocks and 1 ng g^{-1} in soil (4, 5). These levels in real materials are usually lower than the detection limits of an atomic absorption spectrometer. Another problem is matrix interferences (5). To overcome these problems, pre-concentration/separation techniques for gold and other metal ions including adsorption, electro-deposition, cloud point extraction, liquid-liquid extraction, membrane filtration, precipitation, etc. (6-16) have been used for the determination of gold by flame atomic absorption spectrometry.

Microextraction procedures for the enrichment/separation of trace contaminants in environmental samples are very useful and popular at trace levels (17-19) because of their simplicity, high extraction efficiency, and consumption of low levels of toxic organic solvents for green chemistry. Ionic liquids (IL) have some preferred properties such as low vapor pressure, good solubility for inorganic and organic compounds, and non-flammability. Ionic liquids are an alternative to other organic solvents in liquid-liquid extraction techniques (20-24). Some works discuss the application of IL for the enrichment of metals in environmental samples (24-31).

In this work, a preconcentration and separation method has been established based on microextraction of gold(III) at trace levels as its (AuCl_4^-) complex before determination by flame atomic absorption

ABSTRACT

We report on the application of the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate for the micro-extraction and enrichment of gold (in the form of tetrachloroaurate) prior to its determination by flame atomic absorption spectrometry (FAAS). The effects of the concentration of hydrochloric acid, the amount of ionic liquid and the sample volume on the recoveries of gold(III) were studied. The preconcentration factor is 40; the limit of quantification $3.4 \text{ } \mu\text{g L}^{-1}$ for aqueous samples and $0.07 \text{ } \mu\text{g g}^{-1}$ for solid samples. Accuracy was proven by the successful analysis of the standard reference material CDN-GS-3D Gold Ore. The method was applied to the determination of gold in water, soil, and ore samples.

spectrometry. The parameters for the recovery of gold were examined. Based on our literature survey, ionic liquid microextraction of (AuCl_4^-) is performed in this work for the first time.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3110 flame absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used for the determination of gold. A 10-cm burner head, gold hollow cathode lamp, and an air/acetylene flame were used. The operating parameters for the instrument were set as recommended by the manufacturer and are listed in Table I. The samples were

introduced into the nebulizer of the AAS by using a micro-injection unit (32,33). A $100\text{-}\mu\text{L}$ amount of the sample was injected into a mini-homemade Teflon® funnel with an Eppendorf® pipette which was connected to the nebulizer with capillary tubing. The water used was purified in a Model RO-180 (HUMAN Corporation, Seoul, Korea).

Standards and Reagents

All solutions were prepared with reverse osmosis purified water. Acetonitrile, acids, and other chemicals used were obtained from E. Merck, Germany. The calibration curve for gold was established using standard solutions prepared by dilution from 1000 mg L^{-1} gold(III) stock solution (E. Merck). The working standard concentration range was $0.5\text{-}5 \text{ mg L}^{-1}$. The standards were not put through the extraction method. Gold Ore Reference Standard CDN-GS-3D was purchased from CDN Resource Laboratories Ltd. (Canada).

A 0.14-g mL^{-1} amount of 1-hexyl-3-methylimidazolium hexafluorophosphate $[\text{C}_6\text{mim}][\text{PF}_6]$ (No. 490065, Aldrich, Milwaukee, WI, USA) was prepared in acetonitrile. Different concentrations of hydrochloric acid solution (E. Merck, Germany) were prepared in purified water.

TABLE I
Instrumental Settings

Element	Wave-length (nm)	Slit Width (nm)	Lamp Current (mA)
Au	242.8	0.7	15

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Sample Preparation

A 9-mL amount of sample solution containing Au(III) and 1 mL of 1 mol L⁻¹ HCl solution was placed into a 50-mL polypropylene centrifuge tube. Then, 1000 µL of 140 mg [C₆mim][PF₆] in acetonitrile was injected rapidly into the solution by using a 3.0-mL syringe. The cloudy solution was centrifuged for 7.0 minutes at 4000 rpm. The ionic liquid phase settled at the bottom of the centrifuge tube. Then the aqueous phase was separated by a syringe centered in the tube. The lower organic phase was taken and brought to 500-µL volume with concentrated nitric acid. An aliquot of 100 µL of the solution was introduced to the nebulizer of the FAAS using the micro-injection method to determine gold (34,35).

Application to Real Samples

The ionic liquid microextraction method was applied to an ore sample from Sivas, Turkey, and to agricultural soil samples obtained from Yozgat, Turkey. The IL method was also applied to thermal water from Denizli, Turkey, and tap water from Ordu, Turkey.

A 1.00-g amount of ore, or 1.00 g of soil, or 0.25 g of standard reference material CDN-GS-3D Gold Ore (CDN Resource Laboratories, Ltd., Canada) was weighed, placed into a 100-mL beaker, and digested with 20 mL *aqua regia* at 95 °C. The mixture was evaporated to near dryness, mixed with 20 mL of *aqua regia*, and again evaporated to dryness. Then, 5.0 mL of 0.5 mol L⁻¹ HCl was added and the sample mixed with a magnetic stirrer. The mixture was filtered through a blue filter paper. Blank digestions were also performed using the same digestion procedure. Then the microextraction procedure given in the Sample Preparation section was applied.

The water samples were filtered through a Millipore® cellulose

membrane filter (0.45 µm pore size). Then the preconcentration procedure given in the Sample Preparation section was applied to the 15 mL of tap water samples.

RESULTS AND DISCUSSION

Investigation of Experimental Conditions

The effects of the HCl concentration on the recoveries of gold ions as tetrachloroaurate complex were examined at the HCl concentration range of 0.1–1.0 mol L⁻¹. Gold(III) ions were effectively extracted in the range of 0.1–1.0 mol L⁻¹ of HCl. For this work, 0.1 mol L⁻¹ HCl was selected as the optimal HCl concentration.

The effects of the amount of [C₆mim][PF₆] on the retention of gold(III) were also examined and the results are given in Figure 1. The recovery values for gold(III) without [C₆mim][PF₆] were found to be lower than 5%. The recovery values were quantitative (>95%) after addition of 140 mg of ionic liquid. For all further studies, 140 mg of [C₆mim][PF₆] was used.

The influence of sample volume for gold(III) was studied in the 10–40 mL range. Quantitative extraction values were observed between 10 and 20 mL. A precon-

centration factor of 40 was obtained when using 20 mL of starting volume and 0.5 mL of final volume.

The effects of some matrix ions in environmental samples were examined to verify the selectivity of the method for the enrichment and separation of gold as tetrachloroaurate complex (36–43). The results in Table II show that they are suitable for the preconcentration and separation of gold in real samples.

Figures of Merit

The detection limit (LOD) of the proposed method for the determination of gold was studied. The LOD, defined as the concentration equivalent to three times the standard deviation of the blank solution (n=11, XL=3s/PF, XL: limit of detection, PF: preconcentration factor), was 3.4 µg L⁻¹ for aqueous samples and 0.07 µg g⁻¹ for solid samples (41,42).

The limit of quantification (LOQ) for the determination of gold was calculated as three times the detection limit (LOD). The LOQ was 10.2 µg L⁻¹ for aqueous samples and 0.21 µg g⁻¹ for solid samples.

The present procedure was also applied to Gold Ore Reference Standard CDN-GS-3D. While the certified value was 3.41 ± 0.25 µg g⁻¹,

Fig. 1. Influences of amount of ionic liquid (n=3).

the result by the present method was $3.32 \pm 0.20 \mu\text{g g}^{-1}$. The result shows that the certified material is in good agreement with the certified value.

Applications

The IL microextraction method was applied to water and soil samples from various locations in Turkey. The spike tests for gold(III) were performed for thermal and tap waters and agricultural soils from Yozgat, Turkey (Tables III and IV). The results show that good agreement was obtained between the added and found gold concentrations.

The procedure was also applied to an ore sample from Sivas City in Turkey for the determination of its gold level. The gold content was found as $2.1 \pm 0.1 \mu\text{g g}^{-1}$ ($n=6$).

Comparison to Other Preconcentration Techniques

The analytical performance of the microextraction method was found to be comparable to other separation-preconcentration methods for gold (Table V).

TABLE II
Matrix Effects ($n=3$)

Ions	Added as:	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaNO_3	15,000	102 ± 6
K^+	KCl	12,500	100 ± 0
Ca^{+2}	$\text{Ca}(\text{NO}_3)_2$	5000	102 ± 3
Mg^{+2}	$\text{Mg}(\text{NO}_3)_2$	5000	97 ± 2
SO_4^{-2}	Na_2SO_4	5000	109 ± 8
PO_4^{-3}	Na_3PO_4	5000	98 ± 4
Cu^{+2}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	20	97 ± 3
Fe^{+3}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	20	95 ± 0
Ni^{+2}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20	102 ± 3
Co^{+2}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20	100 ± 1
Pb^{+2}	$\text{Pb}(\text{NO}_3)_2$	20	100 ± 3

TABLE III
Spike Test for Microextraction of Gold(III) in Water Samples ($n=3$)

Added (μg)	Tap Water (Ordu)		Thermal Water (Denizli)	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
0.00	< LOQ	-	< LOQ	-
1.00	0.98 ± 0.04	98	1.03 ± 0.03	103
2.00	1.91 ± 0.20	96	1.91 ± 0.09	96

LOQ: Limit of quantification.

TABLE IV
Spike Tests for Gold in Agricultural Soil from Yozgat City ($n=3$)

Added (μg)	Found (μg)	Recovery (%)
0.00	< LOQ	-
1.00	1.0 ± 0.1	99
2.00	1.9 ± 0.1	98

LOQ: Limit of quantification.

TABLE V
Comparison of Preconcentration-Separation Procedures for Gold

System	PF	DL	Literature
Dispersive liquid-liquid microextraction of gold as victoria blue R complex	388	$0.005 \mu\text{g L}^{-1}$	(38)
Amberlite XAD-2000/DDTC	200	$16.6 \mu\text{g L}^{-1}$	(44)
Amidinothioureido-silica gel chelating resin	-	$13 \mu\text{g L}^{-1}$	(45)
Octadecyl silica membrane disks modified with pentathia-15-crown-5	100	$1.0 \mu\text{g L}^{-1}$	(46)
Dowex M-4195 chelating resin	31	$1.61 \mu\text{g L}^{-1}$	(47)
Duolite GT-73 chelating resin	50	$0.085 \mu\text{g L}^{-1}$	(48)
Ionic liquid microextraction of AuCl_4^-	40	$3.4 \mu\text{g L}^{-1}$ for liquids and $0.07 \mu\text{g g}^{-1}$ for solids	This work

PF: preconcentration factor.

DL: Detection Limit.

CONCLUSION

The use of a newly developed ionic liquid-based method for microextraction/enrichment of gold from real samples has been presented, followed by flame atomic absorption spectrometric determination. The proposed method is rapid and simple, selective and sensitive, and uses green chemistry. The effects of matrix ions are tolerable. The procedure would appear to have potential for application in the separation, preconcentration, and determination of gold in other types of geological samples.

ACKNOWLEDGMENT

The authors thank the Unit of the Scientific Research Projects, University of Erciyes, for financial support. Dr. M. Soylak also thanks King Saud University, Riyadh, Saudi Arabia.

Received September 31, 2012.

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