Arabian Journal of Chemistry (2014) 7, 770–774

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Flame atomic absorption spectrometry determination of trace amount of gold after separation and preconcentration onto ion-exchange polyethylenimine coated on Al_2O_3

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Received 1 October 2010; accepted 16 December 2010
Available online 20 December 2010

KEYWORDS

Separation;
Polyethylenimine/Al_2O_3 sorbent;
Solid-phase extraction;
Preconcentration;
Gold determination

Abstract The object of this work is to develop a simple and selective method for efficient extraction of Au(III) ions in aqueous solution using a new solid-phase extraction sorbent. Polyethylenimine (PEI) ion-exchange polymer was coated on alumina in the presence of $NaNO_3$. The method is based on sorption of Au^{3+} ions on 50 mg PEI/Al_2O_3. A solution of 0.5 M thiourea, then 1.0 M HCl effectively eluted the gold ion and then aspirated into flame atomic absorption spectroscopy (FAAS). The influence of flow rate of sample solution and eluent, the pH effect, eluent type and sorption capacity was investigated. The effects of various diverse ions for preconcentration and separation of the gold ion were investigated. Relative standard deviation of 4.0 μg mL^{-1} of gold was 1.46% (n = 10). The detection limit was 26.2 ng L^{-1} in original solution. The method has been applied successfully for the recovery of trace amount of Au(III) ions from water samples.

1. Introduction

For many years, efforts of the analysts focused on the development of the extraction techniques that allow efficient extraction. There are traditional and modern extractions for separation, preconcentration and determination processes of trace metal ions from different matrices. When extracting liquid samples, traditional liquid–liquid extraction faces several limitations, namely use of an extractant non-miscible with the sample, difficulty in extracting polar and ionic compounds from water, large organic solvent volumes resulting in a diluted

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2010.12.018
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extract. To prevent these major drawbacks, solid-phase extraction has been employed (Camel, 2002). The preconcentration procedure is an essential step for the accurate measurement, especially those present in trace level (μg L^{-1} and ng L^{-1}). The most common solid phase extraction (SPE) techniques for preconcentration of metal ions use various adsorbents such as, activated carbon (Ghaedi et al., 2007), cellulose (Burba and Willmer, 1983) amberlit XAD resins (Ferreria et al., 1999), analcime zeolites (Afzali et al., 2007), silica gel (Huang et al., 2008; Akhond et al. 2006), synthetic zeolites (Rios et al., 2008), octadecylsilica membrane disk (Bagheri et al., 2003) and other materials (Absalan et al., 2007; Absalan and Ayatollahi, 2003).

The ion-pair reagents containing bulky anions are often used to form extractable complex ion associates with charged bulky cationic complex species of neutral ligands (Aworn et al., 2005). Because of environmental and economical aspects, some studies were done on selective and effective extractants for toxic and valuable metals from water and soils. Au is known as the precious metal. This term reflects its economic value as well as the rare occurrences of the metals. Some papers have reported preconcentration and recovery of Au(III) in various samples with different kinds of methods (El-Shahawi et al., 2007; Adams, 2003; Zhang and Dreisinger, 2002; Donia et al., 2005; Chakrpani et al., 2001; Moreau and Bond, 2006; Chung and Tabata, 2002; Grosse et al., 2003).

The aim of this work is to develop a rapid and selective method for the extraction of gold(III) in aqueous solution, in level of ng L^{-1}, by using a, new sorbent, water-soluble polymer on alumina that form colored complexes with gold and are determined by flame atomic absorption spectroscopy (FAAS). This work improved the gold extraction techniques. The various parameters such as, pH, eluent solution, volume of sample, interfering ions and flow rates have been evaluated.

2. Experimental

2.1. Apparatus

A Varian model SpectrAA 220 atomic absorption spectrometer (Victoria, Australia, http://www.varianinc.com) was used for measuring of Au(III) in air-acetylene flame. The instrumental parameters according to manufacturer's recommendations are as follows; Wavelength, 242.8 nm; slit width, 1.0 nm; current lamp 4.0 mA; air flow 3.5 L min^{-1} and acetylene flow 1.5 L min^{-1}. Thermo Finnigan Flash EA1112 Microanalyzer was used for the determination of C.H.N percentage. A Metrohm 713 pH meter (http://www.metrohm.de) was used for pH measurement and equipped with a combined glass calomel electrode. Thermogravimetric analysis (TGA) was accomplished on a Perkin–Elmer TGA-USA.

Table 1 Elemental analysis (C.H.N.) for two kinds of sorbent.

Component name	PEI + alumina[a]	PEI + alumina + $NaNO_3$[a]
Nitrogen (%)	1.34594	1.47334
Carbon (%)	1.74820	1.95490
Hydrogen (%)	0.81426	0.84415

[a] Average of two measurements.

2.2. Reagents

All reagents were of analytical grades. The stock solution (1000.0 ng mL^{-1}) of Au(III) was prepared by dissolving appropriate amount of gold chloride (Bombay–New Dehli, Central Drug House) in HNO_3 1:1 and dilute with distilled water to total volume of 50 mL. A 5% solution of polyethylenimine (PEI, molecular weight: 600,000–1,000,000) (Fluka) was prepared in distilled water. The sorbent was Al_2O_3 produced by Fluka. A solution 0.5 M thiourea (Merck) was prepared by dissolving thiourea in distilled water. Analytical grade salts of various metal ions (all from Merck) were of the highest purity available. Buffer solution with pH 5.7 was prepared from 0.1 M CH_3COOH and CH_3COONa.

2.3. Preparation of the sorbent

The coating PEI on alumina (giving PEI/Al_2O_3) was carried out as follows:

1.0 g alumina and 0.5 g $NaNO_3$, with 5 mL PEI 5% were mixed. Then pH was adjusted to 7.2. The obtained suspension was shaken for 24 h. The sorbent that was made, then filtered, rinsed with distilled water several times, and finally dried in desiccators. It was characterized with elemental analysis (C.H.N) and TGA. The thermogravimetric analysis curve of the PEI/alumina sorbent shows a four step mass loss up to 721 °C. The 1.7% mass loss up to 88.6 °C in the first step is due to sorbed water. In the second step mass loss is 3.9% up to 296.4 °C. In the third step mass loss is 3.9%, also, up to 506.5 °C and in the fourth step mass loss is 1.53% up to 723.1 °C. The mass losses in the second, third and fourth steps are corresponding with polyethylenimine. The results of elemental analysis of the dried sorbent showed that on new sorbent N and C elements have existed, thus PEI was coated on alumina (Table 1).

2.4. General procedure

The columns were packed with 50 mg of sorbent (PEI/Al_2O_3) and first was washed with an aliquot of water to wet the surface of the sorbent, then conditioned with a buffer solution at pH 5.7. Then, an aliquot of the sample solution containing of Au(III) (0.5–50.0 μg) was taken in a 50 mL beaker and 3 mL buffer solution was added with pH 5.7. The total volume of the solution was reached to about 30 mL with distilled water. This solution was passed through the column (funnel-tiped glass tube) with flow rate of 2 mL min^{-1}. With this procedure, Au^{3+} ions in water samples were quantitatively adsorbed on the new sorbent and consequently were eluted by 3.0 mL of 0.5 M thiourea and then 2.0 mL of 1.0 M HCl (final volume 5.0 mL) at a flow rate of 4 mL min^{-1}. The final solution was aspirated directly in to the flame AAS against the blank prepared in the same manner without the addition of gold.

3. Results and discussion

3.1. Sorption mechanisms

Polyethylenimine (PEI) is well known for its metal chelation property due to the presence of a large number of amine

groups in a molecule, and is often used to modify the adsorbent surface to increase the adsorption capacity (Ghoul et al., 2003; Deng and Ting, 2005; Sabermahani and Taher, 2006). It is known to exist as a linear structure or a branched structure (Fig. 1).

Commercial branched PEI was employed in this work; it contains primary, secondary and tertiary amino groups in a ratio of approximately 1/4, 1/2 and 1/4, respectively (Amara and Kerdjoudj, 2003). Low-molecular-weight substances can be bound to macromolecules by intermolecular forces, mainly a complex or ionic bond or a combination of both (Molinari et al., 2004). Coating alumina with PEI is a cheap and simple method (one step). By elemental analysis it was observed that prepared sorbent in the neutral media has more capacity than the prepared sorbent in acidic or alkaline media. The experiments showed that the increase in ionic strength causes an increase in the amount of polymer adsorbed on to Al_2O_3 at all measured pH values (Sabermahani and Taher, 2007) $NaNO_3$ is a salt that causes increasing ionic strength. Various amounts of $NaNO_3$ were added to alumina and sorption capacity was measured. The optimum value was determined to be 0.5 g $NaNO_3$ for 1 g alumina.

For gold, by contrast, +3 is the element's best known oxidation state. Au (III) is trend to the oxygen, especially to sulfur and nitrogen. Between various complexes of gold, the square-planar ion $[AuCl_4]^-$ is well-known. Other square-planar ions of the type $[AuX_4]^-$ can be derived in which X = F, Br, I, CN, SCN and NO_3. Numerous cationic complexes have been prepared with amines, both unidentate (e.g. pyridine, quinoline, as well as NH_3) and chelating (e.g. ethylenediamine, bipyridine, phenanthroline) (Greenwood and Earnshaw, 1997). A yellow colored complex has been formed between Au^{3+} and PEI. The eluent also has sulfur and nitrogen groups and Au is complexed with Cl^- in HCl and formed $[AuCl_4]^-$. In

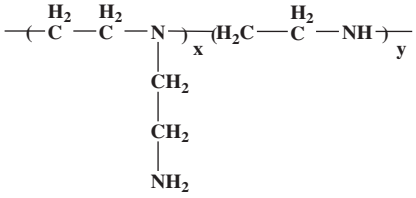

Figure 1 Structure of poly(ethyleneimine) (PEI).

Table 2 Eluent selection.

Elution solution	Recovery (%)
5.0 mL HCl 4.0 M	50.4
5.0 mL thiourea 1.0 M	72.5
5.0 mL SCN^- 0.02 M	2.6
5.0 mL SCN^- 2.0 M	49.0
5.0 mL NH_3 5.0 M	23.7
Acetone in HCl 1 M (1:2.5)	89.2
5.0 mL thiourea 1.0 M in HCl 4.0 M	92.5
5.0 mL thiourea 0.5 in HCl 2.0 M	93.0
5.0 mL $Na_2S_2O_3$ 1.0 M	61.3
3.0 mL thiourea 0.5 M then 2.0 mL HCl 2.0 M	99.8

Conditions and instrumental settings were the same as Fig. 2.

the presence of PEI on alumina the recovery of gold was almost 100%, but with alumina alone, the recovery of Au(III) was 29%.

3.2. Choice of eluent

In order to achieve the maximum recovery for the retained Au(III) ions, by PEI/alumina, various eluents were tested (Table 2). As can be seen from the tests, the best eluent is 3.0 mL of 0.5 M thiourea and then 2.0 mL of 1.0 M HCl.

3.3. Effect of pH

The influence of the pH on the strength of the complexes between Au^{3+} and PEI on alumina was investigated. In order to optimize this parameter, the effect of pH on the recovery of gold was studied in the range 2.0–12 (Fig. 2). Gold was quan-

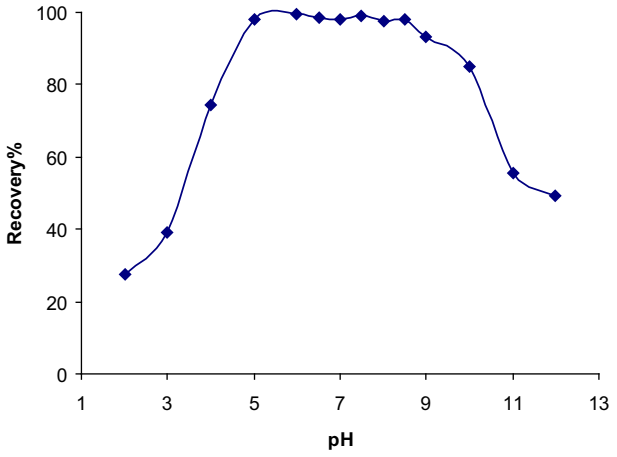

Figure 2 Effect of pH on recovery of gold. Conditions: Au, 20.0 μg; sample flow rate, 2 mL min^{-1}; eluent flow rate, 4 mL min^{-1}; sorbent, 50 mg; final solution, 3.0 mL thiourea 0.5 M then 2.0 mL HCl 1.0 M, instrument settings were as follows; wavelength, 242.8 nm; slit width, 1.0 nm; current lamp 4.0 mA; air flow 3.58 L min^{-1} and acetylene flow 1.5 L min^{-1}.

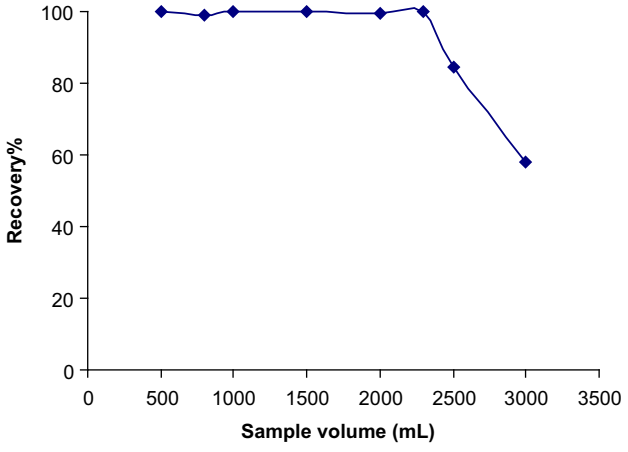

Figure 3 Effect of sample volume on the recovery of gold. Conditions and instrument settings were the same as Fig. 2.

titatively adsorbed in the range of 5.0–8.5. That is almost a wide range. Under pH 5, a majority of amine sites are protonated and can not take part in the chelation process. However, decrease in Au^{3+} recovery in solution of pH > 8.5 is due to the hydrolysis of Au(III). But in the mentioned range a proton of amino groups is in a neutral form, leading to a donor–acceptor interaction with gold ions.

3.4. Effect of flow rates and sample volume

The effect of flow rates of sample and eluent solutions on recovery of Au^{3+} ion was studied. The flow rate of sample solution was examined in the range 0.15–5.0 mL min^{-1} and for the eluent flow rate, the range 0.15-8.0 mL min^{-1} was tested. In the range of 0.15-2.0 mL min^{-1} for the sample solution and 0.15–4.0 mL min^{-1} for the eluent, the flow rate has no significant effect on the recovery of gold. Consequently, all subsequent experiments were performed at 2 mL min^{-1} and 4 mL min^{-1} for flow rates of the sample and eluent, respectively.

To determine the maximum applicable sample volume, solutions containing a fixed amount of Au^{3+} ions (20.0 μg), were varied in the range of 100–3000 mL under the optimum conditions and was passed through a column (Fig. 3). It was observed that the recovery of the analyte was constant up to 2300 mL (break through volume). By using 5.0 mL of the eluent solution, the preconcentration factor was obtained at 460 and it was found to be an excellent factor in contrast to other works for gold.

The maximum capacity of the PEI/alumina sorbent was found 6.0 mg gold per sorbent g. The sorption capacity was determined by the batch process, in the following way: shaking the mixture of 1 g sorbent with various amount of Au^{3+} (1–8 mg), for about 2 h at room temperature.

Table 3 Effect diverse ions.

Ion	Tolerance limit (mg)
Co^{2+}	7
Cr^{6+}, Cu^{2+}	4
Cd^{2+}, Zn^{2+}, Al^{3+}	3
Mn^{2+}, Ni^{2+}, Hg^{2+}	2
Pd^{2+}, Cr^{3+}, Tl^{3+}	1
Pb^{2+}	0.8
Bi^{3+}	0.5
Ag^{+}	0.3

Conditions and instrumental settings were the same as Fig. 2.

Table 4 Analysis of gold in water and standard sample.

Sample	Added (μg)	Found[a] (μg)	Recovery (%)
River water	0.0	B.L.R.[b]	–
	4.0	4.02 ± 0.06	100.5
Spring water	0.0	N.D.[c]	–
	4.0	3.91 ± 0.05	97.8
Tap water	0.0	N.D.	–
	4.0	3.94 ± 0.06	98.5
NKK, No. 1021	0.0	N.D.	–
Alloy[d]	10.0	9.81 ± 0.14	98.1

[a] Average of three determinations, ±S.D.
[b] Below linear range.
[c] Not detected.
[d] The composition of NKK, No. 1021: Si: 5.56, Ni: 0.14, Zr: 0.01, Sn: 0.10, Cu: 2.72, Cr: 0.03, Ca: 0.004, Bi: 0.01, Mg: 0.79, Zn: 1.76, Fe: 0.99, Ti: 0.04, Pb: 0.18, Mn: 0.20 (%).

3.5. Effect of diverse ions

Various salts and metal ions were added to the solution containing 20.0 μg of Au(III) individually. For most of them the tolerance limit was high. An advantage of this sorbent for gold was defined as freedom from high amount of diverse ions (Table 3). It is probably because of this fact that gold is almost a soft cation and the competition between hard cations (included alkaline and alkalin-earth metal) is weak.

3.6. Calibration and sensitivity

Calibration curves for the determination of Au(III) according to optimized conditions were obtained in the linear range of 0.1–10.0 μg mL^{-1}. Calibration curve equation $A = 0.0357c$ (ppm) + 0.0024 with correlation factor of 0.995 was found. The limit of detection (LOD) was calculated as three times the standard deviation (3σ) of 10 replicate measurements of blank sample with the preconcentration step. The detection limit was calculated by dividing the instrumental detection limit by the preconcentration factor. Therefore, the detection limit was obtained 26.2 ng L^{-1} in original solution. Sensitivity for 1% absorbance of gold(III) was obtained at 56.0 μg L^{-1}.

The repeatability of gold ion with PEI/alumina, was also investigated at optimum condition for 10 measurements of

Table 5 Comparative data from some recent studies on preconcentration of gold by using column or batch SPE.

Sorbent	Eluent	Preconcentration factor	Detection limit (μg L^{-1})	Reference
Octadecyl silica membrane disks	0.5 M $S_2O_3^{2-}$	100	1.0	Bagheri et al. (2003)
Amberlite XAD	Acetone	200	32.0	Elci et al. (2003)
Activated Carbon	2 M NH_3 in acetone	20	–	Soylak et. al. (2000)
Aminopropylsilica gel	0.5 M HCl + 0.01 M thiourea	100	4.12	Hassanien and Abou-El-Sherbini (2006)
Amidinothioureido-silica gel chelating resin	5.0% thiourea	–	13.0	Zhang et al. (2002)
Amberlite XAD-2000	1.0 M HNO_3 in acetone	200	16.6	Senturk et al. (2007)
PEI/Alumina	0.5 M thiourea + 1.0 M HCl	460	0.026	This work

4.0 μg mL^{-1} of gold. Relative standard deviation was obtained 1.46% ($n = 10$).

3.7. Analysis of gold in water samples and standard alloys

The applicability of the proposed method was investigated in real samples with different matrices. The result, as the average of four separate determinations is shown in Table 4. Furthermore, standard solution containing Au^{3+} (10.0 μg) was added to the alloy (NKK, No. 1021); the results are also summarized in Table 4. As the table shows, in all cases, the gold recovery is almost quantitative.

3.8. Comparison to other methods

A comparison of the proposed system with other preconcentration procedures using several sorbents is given in Table 5. Preconcentration factor obtained is 460. Thus, it is higher than the presented results reported in the literature. Sorption capacity of the PEI/Al_2O_3 sorbent is 6 mg per sorbent g. The results obtained shows that the proposed method can be applicable for the separation of trace gold ions in a variety of water samples.

4. Conclusions

The adsorbent polyethylenimine/alumina for SPE method of gold extraction is a simple, highly selective and low cost method. The preconcentration factor of 460 was possible and R.S.D. was found to be 1.46% and they are better than the values that were reported in the previous works. The method can be successfully applied to the separation and determination of Au^{3+} in samples with complex matrix and water samples.

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