

Separation and enrichment of gold(III) from environmental samples prior to its flame atomic absorption spectrometric determination

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Abstract

A simple and accurate method was developed for separation and enrichment of trace levels of gold in environmental samples. The method is based on the adsorption of Au(III)–diethyldithiocarbamate complex on Amberlite XAD-2000 resin prior to the analysis of gold by flame atomic absorption spectrometry after elution with $1 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone. Some parameters including nitric acid concentration, eluent type, matrix ions, sample volume, sample flow rate and adsorption capacity were investigated on the recovery of gold(III). The recovery values for gold(III) and detection limit of gold were greater than 95% and $16.6 \mu\text{g L}^{-1}$, respectively. The preconcentration factor was 200. The relative standard deviation of the method was <6%. The adsorption capacity of the resin was 12.3 mg g^{-1} . The validation of the presented procedure was checked by the analysis of CRM-SA-C Sandy Soil certified reference material. The presented procedure was applied to the determination of gold in some environmental samples.

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1. Introduction

Gold, as a global currency, an investment and simply a thing of beauty, is one of the precious metals and held an allure for thousands of years. Gold possesses a unique combination of properties that have resulted in its use in a wide range of industrial applications [1]. Cyanide, as a leaching agent, is commonly used in industrial gold extraction [2,3]. The recovery of gold by the adsorption of auro-cyanide complexes onto activated carbon is a well-established process [4]. However, great interest in the use of non-cyanide methods for the dissolution of gold arises from concerns regarding the toxicity of cyanide and the inability of cyanide solution to effectively leach carbonaceous or complex ores. Also, these conventional industrial processes for recovering precious metals generally consist of multiple steps

of dissolution, conditioning and precipitation. These processes are not only labor-intensive but also time-consuming, and hence much work has been conducted on the development of alternative methods [5].

The concentration of gold in environmental, geological and metallurgical materials is usually too low to be determined directly by AAS owing to insufficient sensitivity and matrix interferences. Hence, separation and enrichment of analyte are important aspects in determination of gold in addition to the effect of other trace metal ions in saline matrices [6–9]. For this purpose, several separation and enrichment techniques for gold (and for trace metal ions) including solvent extraction [10–12], co-precipitation [13–15], sorption, [16–20] etc., have been developed. One of this technique, solid-phase extraction (SPE) by Amberlite resins has been widely used for separation and enrichment of almost all the other trace metals, besides gold [21–29].

Sodium diethyldithiocarbamate (Na-DDTC) is a well-characterised reagent that reacts with over many metal ions such as Au, Cu, Fe, Pb, Mn, Zn, Cd, Ni, Bi and Cr to form very stable

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complexes [6,7]. These chelates have been used for the solid-phase extraction of some metal ions from aqueous solutions [6,7,28,29].

In this study, a solid-phase extraction method for gold(III)-diethyldithiocarbamate on Amberlite XAD-2000 resin has been presented. The conditions including nitric acid concentration, amounts of reagents, eluent type, sample volume for the quantitative recoveries for gold(III) were investigated.

2. Experimental

2.1. Instrumentation

A Unicam AA-929 model atomic absorption spectrometer (AAS) equipped with single hollow cathode lamp (6.0 mA current for gold) and 5 cm of burner head was operated the determinations. Gold ions in solution were atomized by air/acetylene mixture. Wavelength was set at 242.8 nm and the spectral bandwidth at 0.5 nm for gold.

Milestone Ethos D microwave digestion unit with closed vessels and 1450 psi max pressure was used for digestion of ore and soil materials.

2.2. Reagents and solutions

All reagents were of analytical reagent grade and purchased from Merck and Fluka. Stock solution of Au(III) with a concentration of 1000 mg L^{-1} in 2.0 mol L^{-1} HCl was used. Model and standard solutions were prepared by diluting this stock solution using suitable ratios. Distilled-deionized water was used in all experiments.

Amberlite XAD-2000 resin ($600 \text{ m}^2 \text{ g}^{-1}$ surface area and 20–50 mesh particle size) and Sodium diethyldithiocarbamate (Na-DDTC) were supplied by Sigma Chem. Gold in sandy soil standard (CRM-SA-C) from High-Purity Standards, Inc., was used as standard reference material.

2.3. Preparation of the mini column

Amberlite XAD-2000 resin was thoroughly washed with 1 mol L^{-1} NaOH, water, 1 mol L^{-1} HNO₃, water and acetone successively. It was finally washed with 10 mL of water and dried in desiccators for further use.

A glass column with stopcock and porous disk (1 cm × 10 cm i.d.) was used in all experiments. The glass column was loaded with 0.250 g of ground and sieved (150–200 μm) Amberlite XAD-2000 resin. After each use, the resin filled to column was washed with large volumes of distilled-deionized water and 1 mol L^{-1} HNO₃ in acetone, and was conditioned with HNO₃ solutions in different concentrations before being stored in water for the next experiment.

2.4. Preconcentration procedure

Fifty milliliters of distilled water containing 50 μg of Au(III) ions were prepared in $0.5\text{--}2.5 \text{ mol L}^{-1}$ HNO₃. Then 5 mL of Na-DDTC (0.1%) was added to the solution. The solution was

passed through the column at 10.0 mL min^{-1} . The adsorbed gold complex on the column was eluted with 1 mol L^{-1} HNO₃ in acetone and acetone in the eluent was evaporated to near dryness. The residue was diluted to 5.0 mL with 1 mol L^{-1} HNO₃ and the final solution was analyzed for gold by FAAS.

2.5. Application to real samples

The proposed method was applied to CRM-SA-C Sandy Soil, Mastra Gold Ore from Gumushane, Turkey and agricultural soil from Surmene, Trabzon, Turkey. The 1.250 g of fine powdered samples were digested in microwave digestion unit by addition of 8 mL of aqua regia and 1 mL of HF according to the microwave digestion program under 45 bar pressure (1 min for 250 W and 180 °C, 1 min for 0 W and 180 °C, 10 min for 650 W and 200 °C, 5 min for 250 W and 220 °C, respectively, vent: 3 min). The final mixture was evaporated to dryness in a hot plate. Twenty milliliters of 1 mol L^{-1} HNO₃ was added. The suspension formed was filtered through blue band filter paper. Then the enrichment procedure given in Section 2.4 was applied.

Another application of the presented procedure was performed to a mineral water from Araklı, Trabzon, Turkey and stream water from Of, Trabzon, Turkey. Fifty milliliters of water sample was taken then the procedure given above was applied.

3. Results and discussion

3.1. Effect of nitric acid concentration

The metal–diethyldithiocarbamate complexes were generally occurred at the acidic media [30]. The influence of nitric acid concentration on the retention of gold(III) and other some metal ions–diethyldithiocarbamate chelates on Amberlite XAD-2000 was studied in the HNO₃ concentration range of $0.5\text{--}2.5 \text{ mol L}^{-1}$. The results are depicted in Fig. 1. Gold(III)-diethyldithiocarbamate chelates was quantitatively recovered in all working range of nitric acid concentration. Gold(III) was effectively separated from other metal ions simultaneously in the $1.0\text{--}2.5 \text{ mol L}^{-1}$ HNO₃ concentrations. Hence, 2.0 mol L^{-1} HNO₃ medium was selected for the next applications in order to

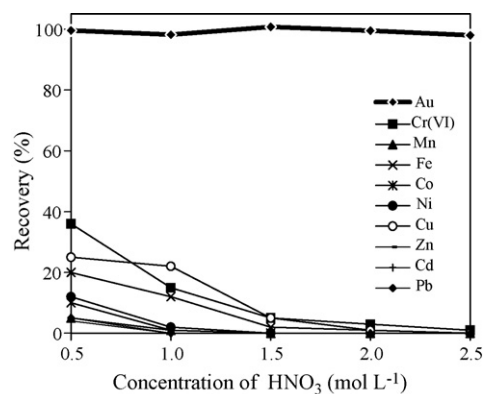


Fig. 1. The variation of HNO₃ concentration with recovery (eluent: 1 mol L^{-1} HNO₃ in acetone, resin quantity: 0.250 g, sample flow rate: 10 mL min^{-1} , $N=4$).

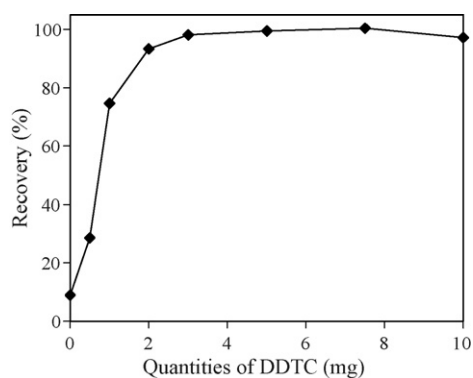


Fig. 2. Effect of DDTC quantities on the recovery of gold(III).

separate gold ions from other metal ions and to preconcentration of gold(III).

3.2. Effect of DDTC quantities on the recovery of gold

The influences of quantities of DDTC as a chelating agent on the solid-phase extraction of gold(III) were investigated. The quantity of DDTC on the retention was examined from 0 to 10 mg. The results are given in Fig. 2. The recoveries without ligand were below 10%. The recovery values increased with the addition of DDTC. The quantitative recovery values were obtained after 2.0 mg of DDTC (Fig. 2). After this point the recoveries were quantitative and constant in all working range. For all further works, 5.0 mg of DDTC (5.0 mL of 0.1%) was added.

3.3. Effect of eluent

To desorption gold(III) from the Amberlite XAD-2000 column, various eluents were examined. The results were given in Table 1. Due to gold(III) forms strong complexes with I^- , $S_2O_3^{2-}$, CN^- , $(NH_2)_2CS$ and SCN^- [3,22,31,37], the various solution of these ions were also examined as eluting agent. As can be seen in Table 1, the recoveries of gold ions were not quantitative when I^- , $S_2O_3^{2-}$, CN^- , $(NH_2)_2CS$ and SCN^- as eluent. The best eluent for gold(III) on the resin was 10 mL of 1 mol L⁻¹ HNO₃ in acetone. Thus, 1 mol L⁻¹ HNO₃ in acetone was used in the next applications as eluent.

Table 1

The results of the recovery of gold by different eluent types (2 mol L⁻¹ HNO₃ medium, resin quantity: 0.250 g, $N=4$)

| Eluent type | Volume (mL) | Recovery (%) |
|---|-------------|--------------|
| 0.5 mol L ⁻¹ KSCN | 20 | <5 |
| 0.3 mol L ⁻¹ KI in water-methanol | 5-5 | 69 ± 3 |
| 0.5 mol L ⁻¹ Na ₂ S ₂ O ₃ | 20 | 13 ± 1 |
| 0.5 mol L ⁻¹ (NH ₂) ₂ CS | 20 | <5 |
| 1.0 mol L ⁻¹ KCN | 10 | 37 ± 1 |
| 1.0 mol L ⁻¹ KI-1.0 mol L ⁻¹ KCN | 5-5 | 40 ± 2 |
| 1.0 mol L ⁻¹ HNO ₃ | 10 | <5 |
| 1.0 mol L ⁻¹ HNO ₃ in acetone | 10 | 100 ± 3 |
| 1.0 mol L ⁻¹ HNO ₃ in ethanol | 10 | 88 ± 3 |
| Acetone | 10 | 54 ± 2 |

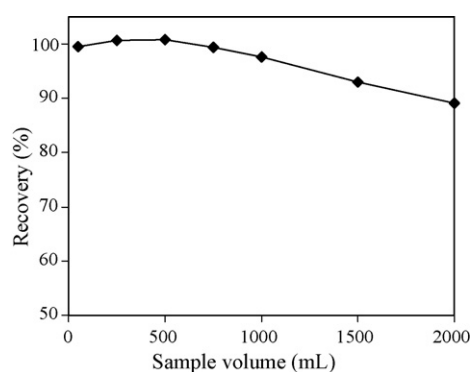


Fig. 3. The variation of sample volume with recovery.

3.4. Effect of sample volume on the recovery of gold

Because of low concentrations in real samples, large sample volume is generally required for effective preconcentration and determination of gold. Therefore, the optimum sample volume and recovery were investigated by using model solutions containing the same amount of gold in the volume range of 50–2000 mL, which were passed through the column under optimal conditions. The recoveries were found to be quantitative and stable until 1000 mL (Fig. 3). The enrichment factor was established as 200 in optimized conditions (sample and final eluent volumes were 1000 and 5 mL, respectively).

3.5. Effect of sample flow rate

The flow rate of the model solutions through the column is one of the factor affecting the length of time needed for the determination of gold-DDTC chelates and is directly related to the contact of the gold-DDTC chelates with the resin. As a result of the investigation of this effect, valuable information about the adsorption rate of the complexes on the resin can be obtained. Hence, model solutions of 50 mL were passed through the column with flow rates in the range 1–25 mL min⁻¹, where vacuum was applied with a waterjet. It was observed that the recovery did not change until 25 mL min⁻¹; hence a flow rate of 10.0 mL min⁻¹ was selected for the experiments.

3.6. Effect of matrix ions

The determination of gold is rather difficult in geological samples due to the high concentrations of other elements such as Na, Fe, Cu, Pb, Ni and Zn. Therefore, model solutions containing fixed amount of gold together with either individual matrix metals or mixed matrix metals (Na, K, Ca, Mg, Fe, Cu, Ni, Pb and Zn) were prepared and the preconcentration procedure was applied. Since there is an excess amount of matrix elements in the medium, in order to prevent the contamination of the eluent by these metals, the resin was washed with 10 mL of 1 mol L⁻¹ HNO₃ prior to elution. The results are given in Tables 2 and 3. The results showed that the recovery of gold was not affected by the medium composition containing either individual or mixed metals. Thus, gold was both separated from other matrix metals and pre-concentrated successfully.

Table 2

The results of the recovery of gold from the medium containing combined matrix ions (Fe, Cu, Ni, Pb, Zn, Cr, Na, K, Ca, Mg)

| Combined foreign metal ions (mg L ⁻¹) | Au | | |
|---|-----------------------------|-----------------------------|--------------|
| | Added (mg L ⁻¹) | Found (mg L ⁻¹) | Recovery (%) |
| 0 | 1.00 | 1.00 ± 0.03 | 100 |
| 50 | 1.00 | 1.01 ± 0.04 | 101 |
| 125 | 1.00 | 1.02 ± 0.05 | 102 |
| 250 | 1.00 | 1.02 ± 0.03 | 102 |
| 500 | 1.00 | 1.01 ± 0.02 | 101 |
| 1000 | 1.00 | 1.00 ± 0.03 | 100 |

3.7. Adsorption capacity of the resin

The adsorption capacity is the maximum metal quantity taken up by 1 g of resin and given by mg metal g⁻¹ resin or meg (miliequivalent gram). Langmuir adsorption isotherm is one of the most well known and applied adsorption isotherms and described by the equation below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{a_L q_{\max}} \quad (1)$$

where q_e is the amount of metal adsorbed per unit weight of the resin (mg g⁻¹) at equilibrium, C_e the final concentration in the solution (mg L⁻¹), q_{\max} the maximum adsorption at monolayer coverage (mg g⁻¹) and a_L is the adsorption equilibrium constant which is related to energy of adsorption (L mg⁻¹). A plot of C_e/q_e versus C_e shows linearity, hence Langmuir constants q_{\max} and a_L can be calculated from the gradient and intercept of the plot.

In order to determine the resin capacity, 50–5000 µg of Au(III) were loaded to the column containing 250 mg of resin and recoveries were investigated. After the concentration of 1500 µg, a decrease was observed for the recovery of gold. Then, Langmuir isotherms were plotted in order to determine the resin capacity (Fig. 4). The maximum amount of gold (q_{\max}) adsorbed on 1.0 g and the adsorption equilibrium constant (a_L) were calculated as, 12.3 mg g⁻¹ and $\sim 5 \times 10^4$ L mol⁻¹, respectively, from the plots obtained from gold adsorption.

3.8. Analytical performance of the method

The detection and quantification limit (LOD and LOQ) for gold(III) were determined by passing a 50 mL of blank solution

Table 3

The results of the recovery of gold from the medium containing individual matrix ions (C_{Au} : 1.00 µg mL⁻¹)

| Individual metal ion (mg L ⁻¹) | Recovery of Au (%) | | | | | | | | | |
|--|--------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | Fe | Cu | Ni | Pb | Zn | Cr | Na | K | Ca | Mg |
| 50 | 100 ± 4 | 99 ± 4 | 100 ± 4 | 97 ± 5 | 100 ± 4 | 100 ± 3 | 100 ± 4 | 99 ± 4 | 101 ± 3 | 99 ± 3 |
| 125 | 100 ± 4 | 100 ± 5 | 97 ± 4 | 98 ± 3 | 101 ± 4 | 100 ± 3 | 101 ± 4 | 99 ± 4 | 101 ± 4 | 101 ± 5 |
| 250 | 99 ± 3 | 100 ± 5 | 98 ± 4 | 100 ± 3 | 100 ± 3 | 99 ± 4 | 100 ± 4 | 99 ± 4 | 101 ± 4 | 101 ± 4 |
| 500 | 99 ± 5 | 98 ± 4 | 100 ± 4 | 99 ± 3 | 100 ± 4 | 99 ± 4 | 100 ± 3 | 100 ± 4 | 100 ± 4 | 100 ± 4 |
| 1000 | 99 ± 4 | 100 ± 3 | 101 ± 5 | 99 ± 4 | 100 ± 4 | 100 ± 3 | 99 ± 3 | 101 ± 4 | 100 ± 4 | 101 ± 3 |
| 5000 | 101 ± 6 | – | – | – | – | – | – | – | – | – |

(–), Not worked.

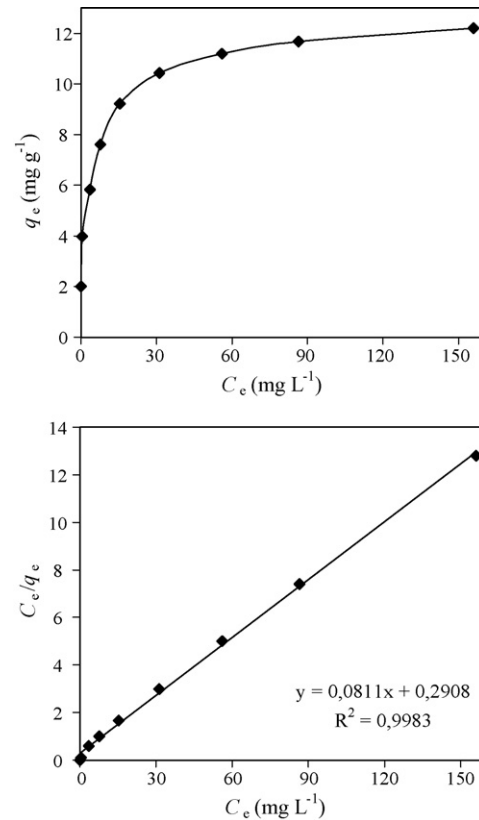


Fig. 4. Langmuir adsorption isotherms for gold.

through the column loaded with Amberlite XAD-2000 resin. The gold content was desorbed from the column with the eluent and 5.0 mL of the eluent was analyzed by FAAS. The detection limit (blank + 3σ, where σ is standard deviation of blank estimation) was 16.6 µg L⁻¹, and the corresponding quantification limit (blank + 10σ) was 36.5 µg L⁻¹. The precision of the method, evaluated as the relative standard deviations obtained after analyzing a series of 10 replicates, was <6% for gold with a concentration of 1.0 µg mL⁻¹.

3.9. Applications

The accuracy of results was verified by analyzing the standard reference material, CRM-SA-C Sandy Soil. The results are given in Table 4. The results found were in good agreement with the certified values of CRMs.

Table 4

Determination of gold in standard reference material, CRM-SA-C Sandy Soil, for accuracy test of the method (sample quantity (g): 0.5, $N=4$)

| Certified value ($\mu\text{g g}^{-1}$) | Found value ($\mu\text{g g}^{-1}$) | Recovery (%) |
|--|--------------------------------------|--------------|
| 25.5 \pm 0.1 | 25.8 \pm 1.5 | 101 |

Table 5

Determination of gold in Mastra Gold Ore (eluent: 1 mol L⁻¹ HNO₃ in acetone, sample quantity (g): 1.250, resin quantity (g): 0.250, final eluent volume: 5 mL, $N=5$)

| Added ($\mu\text{g g}^{-1}$) | Found ^{a,b} ($\mu\text{g g}^{-1}$) | Recovery (%) |
|--------------------------------|---|--------------|
| – | 25.0 \pm 1.4 | – |
| 20 | 45.2 \pm 1.6 | 101 |
| 40 | 64.4 \pm 1.6 | 99 |
| 60 | 84.0 \pm 3.2 | 98 |
| 80 | 104.0 \pm 4.0 | 99 |

The other metal contents of Mastra Gold Ore determined by ACME analytical Lab. are as follows ($\mu\text{g g}^{-1}$, R.S.D.: <5%): Si: 40.2%, Fe: 3.8%, Mg: 900, Ca: 2360, Na: 150, K: 1330, Mn: 77, Cr: 470, Ni: 199, Cu: 3519, Co: 14.3, Pb: 3799, Zn: 2639, As: 749, Cd: 21.6, Sb: 11.8, Bi: 5.9, Sn: 1.0, Ag: 8.6, Mo: 17.0.

^a At the 95% confidence level, R.S.D.: 5.8%.

^b Gold content of Mastra Gold Ore sample was determined as 26.0 $\mu\text{g g}^{-1}$ (R.S.D.: <5%) by ACME Analytical Lab. (ISO 9002 Accredited Co.).

The proposed method was applied to Mastra Gold Ore, Gumushane/Turkey and agricultural soil from Sürmene, Trabzon, Turkey in the optimum conditions. The results were given in Table 5 for Mastra Gold Ore and in Table 6 for agricultural soil. Also the method was applied to mineral water from Araklı, Trabzon, Turkey and stream water from Of, Trabzon, Turkey (Table 7). As seen from Tables 5–7, good agreement was observed between the added and recovered analyte content using the proposed procedure, and the recoveries of gold were >95%. Thus, these results confirm that the procedure is independent from matrix interferences.

Table 6

Results of spiked recoveries of the method (sample quantity (g): 1.250, final eluent volume: 5 mL, $N=3$)

| Added ($\mu\text{g g}^{-1}$) | Agricultural soil from Sürmene, Trabzon, Turkey | |
|--------------------------------|---|--------------|
| | Found ($\mu\text{g g}^{-1}$) | Recovery (%) |
| – | ND | – |
| 20 | 19.2 \pm 1.6 | 96 |
| 40 | 40.4 \pm 2.0 | 101 |
| 60 | 58.0 \pm 2.4 | 97 |
| 80 | 78.4 \pm 2.8 | 98 |

Table 7

Results of spiked recoveries of the method (sample volumes: 50 mL, final eluent volume: 5 mL, $N=3$)

| Added (mg L ⁻¹) | Mineral water from Araklı, Trabzon, Turkey | | Stream water from Of, Trabzon, Turkey | |
|-----------------------------|--|--------------|---------------------------------------|--------------|
| | Found (mg L ⁻¹) | Recovery (%) | Found (mg L ⁻¹) | Recovery (%) |
| – | ND | – | ND | – |
| 0.50 | 0.48 \pm 0.03 | 97 | 0.51 \pm 0.02 | 102 |
| 1.00 | 0.98 \pm 0.04 | 98 | 1.00 \pm 0.04 | 100 |
| 1.50 | 1.52 \pm 0.04 | 101 | 1.47 \pm 0.03 | 98 |
| 2.00 | 1.95 \pm 0.04 | 98 | 2.02 \pm 0.08 | 101 |

4. Conclusion

The Amberlite XAD-2000/DDTC column preconcentration and separation system was proposed for the determination of trace amounts of gold in samples with complicated and variable matrices such as geological samples for its simplicity, high efficiency, good selectivity and accuracy. Most of the metals including iron did not influence the gold determination hence gold was not only preconcentrated successfully but also separated effectively from the other matrix metals. A comparison of the proposed system with other preconcentration procedures is given in Table 8. Enrichment factor (EF) and limit of detec-

Table 8

Procedures for separation and enrichment of gold using column or batch SPE methods and detection by FAAS

| System | Medium | Stripping agent | EF | LOD ($\mu\text{g L}^{-1}$) | References |
|--|--|---|-----|------------------------------|------------|
| Amberlite XAD-16/HCl, column | pH 2 | 0.3 mol L ⁻¹ KI + methanol | 75 | 46.0 | [22] |
| Amberlite XAD-16/HCl-NaI, column | 1.0 mol L ⁻¹ HCl | Acetone | – | 40 $\mu\text{g kg}^{-1}$ | [25] |
| Amberlite XAD-7/KI, column | 2 mol L ⁻¹ HCl | Acetone | 200 | 32.0 | [27] |
| Activated Carbon/dithiophosphoric acid <i>O,O</i> -diethyl ester, column | 0.1 mol L ⁻¹ HCl | 2 mol L ⁻¹ NH ₃ in acetone | 20 | – | [32] |
| Aminopropylsilica gel/morin, batch | pH 2.2 | 0.5 mol L ⁻¹ HCl + 0.01 mol L ⁻¹ thiourea | 100 | 4.12 | [33] |
| Duolite GT-73/HCl, batch | 0.01 mol L ⁻¹ HCl | 0.8 mol L ⁻¹ thiourea + 3.0 mol L ⁻¹ HCl | – | – | [34] |
| Isodiphenylthiourea immobilized silica gel, column | 1.0 mol L ⁻¹ HCl | 2.0% thiourea in 0.5 mol L ⁻¹ HNO ₃ | – | 3.2 | [35] |
| Amidinothioureido-silica gel chelating resin, column | 0.1–6.0 mol L ⁻¹ HCl | 5.0% thiourea | – | 13.0 | [36] |
| Octadecyl silica membrane disks modified by pentathia-15-crown-5, disk | pH 4.5–7.0 | 0.5 mol L ⁻¹ S ₂ O ₃ ²⁻ | 200 | 1.0 | [37] |
| Amberlite XAD-2000/DDTC, column | 2.0 mol L ⁻¹ HNO ₃ | 1.0 mol L ⁻¹ HNO ₃ in acetone | 200 | 16.6 | This work |

LOD, limit of detection; EF, enrichment factor; SPE, solid-phase extraction.

tion obtained were comparable to those presented by other methods described in the literature. As seen from the data in Table 8, the proposed method developed by using Amberlite XAD-2000/DDTC system has high enrichment factor and relatively low LOD when compared to other methods reported in Table 8. CN^- has been widely used to isolate gold from geological samples. However, it is a threat to the environment since it transforms into HCN as a result of the decrease of the pH to values below 9. The current gold isolation processes are complicated and time-consuming therefore novel methods are in great demand to overcome these difficulties. Thus, our method can be proposed as an environmentally friendly alternative compared to the cyanide method.

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References

- [1] World Gold Council, The World of Gold, <http://www.gold.org/index.html>, August 22, 2005.
- [2] D.S.R. Murthy, Microbially enhanced thiourea leaching of gold and silver from lead-zinc sulphide flotation tailings, *Hydrometallurgy* 25 (1990) 51–60.
- [3] A. Aworn, P. Thiravetyan, W. Nakbanpote, Recovery of gold from gold slag by wood shaving fly ash, *J. Colloid Interf. Sci.* 287 (2005) 394–400.
- [4] J. Marsden, I. House, *The Chemistry of Gold Extraction*, Horwood, New York, 1992.
- [5] T. Kinoshita, S. Akita, S. Ozawa, S. Nii, F. Kawaizumi, K. Takahashi, A study on gold(III) recovery via foam separation with nonionic surfactant in batch mode, *J. Miner. Mater. Charact. Eng.* 2 (2003) 71–82.
- [6] A. Mizuike, *Enrichment Techniques for Inorganic Trace Analysis*, Springer-Verlag, Berlin, Heidelberg, 1983.
- [7] J. Minczewski, J. Chwastowska, D. Dybezynski, *Separation and Preconcentration Methods in Inorganic Analysis*, Ellis Horwood, Chichester, 1982.
- [8] M.D. Ye, M.J. Lin, Determination of trace gold by flow injection on-line preconcentration flame atomic absorption spectrometry with trioctylaminelevextrel resin, *Spectrosc. Spectr. Anal.* 24 (2004) 1270–1272.
- [9] S. Haribabu, K. Suvardhan, K. Suresh Kumar, K.M. Reddy, D. Rekha, P. Chiranjeevi, The facile flow-injection spectrophotometric detection of gold (III) in water and pharmaceutical samples using 3,5-dimethoxy-4-hydroxy-2-aminoacetophenone isonicotinoyl hydrazone (3,5-DMHAAINH), *J. Hazard. Mater.* 120 (2005) 213–218.
- [10] P.A. Riveros, Studies on the solvent extraction of gold from cyanide media, *Hidrometallurgy* 24 (1990) 135–156.
- [11] J. Jiang, Y. He, H. Gao, J. Wu, Solvent extraction of gold from alkaline cyanide solution with a tri-*n*-octylamine/tri-*n*-butyl phosphate/*n*-heptane synergistic system, *Solvent Extr. Ion Exch.* 23 (2005) 113–129.
- [12] M. Murakami, T. Takada, Comparative study of IBMK and DIBK as extraction solvents in strongly acidic media: extraction behavior and kinetic stability of $\text{Cu}(\text{PCD})_2$ in these solvents, *Talanta* 37 (1990) 229–232.
- [13] S.E. Jackson, B.J. Fryer, W. Gosse, D.C. Healey, H.P. Longrich, D.F. Strong, Determination of the precious metals in geological materials by inductively coupled plasma-mass spectrometry (ICP-MS) with nickel sulphide fire-assay collection and tellurium coprecipitation, *Chem. Geol.* 83 (1990) 119–132.
- [14] M. Khoudiakova, M.C. Gupta, S. Deevib, $\text{Au}/\text{Fe}_2\text{O}_3$ nanocatalysts for CO oxidation: a comparative study of deposition-precipitation and coprecipitation techniques, *Appl. Catal. A-Gen.* 291 (2005) 151–161.
- [15] M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples, *Talanta* 66 (2005) 1098–1102.
- [16] N. Rajesh, B. Deepthi, A. Subramaniam, Solid-phase extraction of chromium(VI) from aqueous solutions by adsorption of its ion-association complex with cetyltrimethylammoniumbromide on an alumina column, *J. Hazard. Mater.* 144 (2007) 464–469.
- [17] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000, *J. Hazard. Mater.* 146 (2007) 155–163.
- [18] S.L.C. Ferreira, H.M.C. Andrade, H.C. dos Santos, Characterization and determination of the thermodynamic and kinetic properties of the adsorption of the molybdenum(VI)-calmagite complex onto active carbon, *J. Colloid Interf. Sci.* 270 (2004) 276–280.
- [19] A.A. Ensafi, T. Khayamian, M.H. Karbasi, Online preconcentration system for lead(II) determination in waste water by atomic absorption spectrometry using active carbon loaded with pyrogallol red, *Anal. Sci.* 19 (2003) 953–956.
- [20] V.A. Lemos, P.X. Baliza, J.S. Santos, L.S. Nunes, A.A. de Jesus, M.E. Rocha, A new functionalized resin and its application in preconcentration system with multivariate optimization for nickel determination in food samples, *Talanta* 66 (2005) 174–180.
- [21] S. Baytak, A.R. Turker, Flame Atomic Absorption Spectrometric determination of manganese in alloys after preconcentration onto amberlite XAD-4 loaded with *Saccharomyces carlsbergensis*, *Turk. J. Chem.* 28 (2004) 243–253.
- [22] J.D. Kumar, D. Rekha, K. Suvardhan, P.R. Prasad, B.K. Priya, B.C.V. Reddy, P. Chiranjeevi, Copper (II) preconcentration on Amberlite XAD-2010 loaded micro organisms prior to its spectrophotometric determination, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2007.03.040, in press.
- [23] L. Elci, M. Soylak, E.B. Buyuksekerici, Separation of gold, palladium and platinum from metallurgical samples using an amberlite XAD-7 resin column prior to their atomic absorption spectrometric determinations, *Anal. Sci.* 19 (2003) 1621–1624.
- [24] T. Saitoh, S. Suzuki, M. Hiraide, Solid phase extraction of some precious metals from hydrochloric acid to polystyrene-divinylbenzene porous resin impregnated with polyoxyethylene-type nonionic surfactant, *J. Chromatogr. A* 1097 (2005) 179–182.
- [25] L. Elci, M. Soylak, A. Uzun, E. Buyukpatir, M. Dogan, Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin, *Fresen. J. Anal. Chem.* 368 (2000) 358–361.
- [26] D. Rekha, J.D. Kumar, B. Jayaraj, Y. Lingappa, P. Chiranjeevi, Nickel(II) determination by spectrophotometry coupled with preconcentration technique in water and alloy samples, *Bull. Korean Chem. Soc.* 28 (2007) 373–378.
- [27] S.A. Rocha, S.L.C. Ferreira, A procedure of separation and preconcentration for titanium determination in seawater samples by ICP-OES, *Eurasian J. Anal. Chem.* 2 (2007) 1–11.
- [28] C. Duran, H.B. Senturk, A. Gundogdu, V.N. Bulut, L. Elci, M. Soylak, M. Tufekci, Y. Uygur, Determination of some trace metals in environmental samples by flame AAS following solid phase extraction with Amberlite XAD-2000 resin after complexing with 8-hydroxyquinoline, *Chinese J. Chem.* 25 (2007) 196–202.
- [29] V.N. Bulut, C. Duran, M. Tufekci, L. Elci, M. Soylak, Speciation of Cr(III) and Cr(VI) after column solid phase extraction on Amberlite XAD-2010, *J. Hazard. Mater.* 143 (2007) 112–117.
- [30] Z.B. Alfasi, C.M. Wai, *Preconcentration Techniques for Trace Elements*, CRC press, Boca Raton, Ann Arbor, London, 1992.
- [31] P. Pohl, B. Prusisz, On the applicability of Duolite GT-73 to column preconcentration of gold and palladium prior to determination by inductively coupled plasma atomic emission spectrometry, *Microchim. Acta* 150 (2005) 159.
- [32] M. Soylak, L. Elci, M. Dogan, A sorbent extraction procedure for the preconcentration of gold, silver and palladium on an activated carbon column, *Anal. Lett.* 33 (2000) 513–525.
- [33] M.M. Hassamien, K.S. Abou-El-Sherbini, Synthesis and characterisation of morin-functionalised silica gel for the enrichment of some precious metal ions, *Talanta* 68 (2006) 1550–1559.

- [34] M. Iglesias, E. Antico, V. Salvado, Recovery of palladium(II) and gold(III) from diluted liquors using the resin duolite GT-73, *Anal. Chim. Acta* 381 (1999) 61–67.
- [35] P. Liu, Z. Su, X. Wu, Q. Pu, Application of isodiphenylthiourea immobilized silica gel to flow injection on-line microcolumn preconcentration and separation coupled with flame atomic absorption spectrometry for interference-free determination of trace silver, gold, palladium and platinum in geological and metallurgical samples, *J. Anal. Atom. Spectrom.* 17 (2002) 125–130.
- [36] S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, Synthesis of amidinothioureido-silica gel and its application to flame atomic absorption spectrometric determination of silver, gold and palladium with on-line preconcentration and separation, *Anal. Chim. Acta* 452 (2002) 223–230.
- [37] M. Bagheri, M.H. Mashhadizadeh, S. Razee, Solid phase extraction of gold by sorption on octadecyl silica membrane disks modified with pentathia-15-crown-5 and determination by AAS, *Talanta* 60 (2003) 839–844.