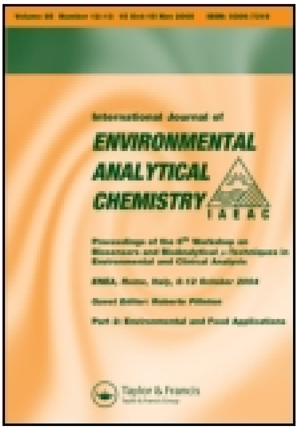

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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To cite this article: Mustafa Soylak & Yunus Emre Unsal (2011): Double-walled carbon nanotubes as a solid phase extractor for separation-preconcentration of traces of gold from geological and water samples, International Journal of Environmental Analytical Chemistry, 91:5, 440-447

To link to this article: http://dx.doi.org/10.1080/03067310903428735

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 5, 20 April 2011, 440–447

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Double-walled carbon nanotubes as a solid phase extractor for separation-preconcentration of traces of gold from geological and water samples

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(*Received 12 June 2009; final version received 19 October 2009*)

In this work, a solid phase extraction method has been developed using a column filled with double-walled carbon nanotubes (DWNT) for preconcentration-separation of gold(III) ions prior to their flame atomic absorption spectrometric determination. Gold(III) ions were quantitatively recovered on DWNT in 1.0 mol L^{-1} HCl. The influences of the analytical conditions including eluent type, sample volume, etc. on the recoveries of gold(III) ions were examined. The effects of concomitant ions were also investigated. The detection limits for gold(III) based on 3σ was calculated as 1.5 $\mu g\,L^{-1}$. The procedure presented in this paper was applied to the gold content of a number of water, geological and anodic slime samples with successful results.

Keywords: double-walled carbon nanotubes; solid phase extractor; gold; separation; atomic absorption spectrometry

1. Introduction

Gold is one of the most precious elements in the world owing to its usage in the jewellery industry [1–4]. The gold content of earth is relatively low and distributed heterogeneously [5–7]. Its products are extensively used in various areas such as the petrochemical industry, medicine and the electronics and nuclear power industries [8–10]. The determination of gold at trace levels in environmental samples including geological and water samples often requires some pretreatment step such as preconcentration-separation [11–14]. Matrix components of the real samples may cause interferences, and the preconcentration procedure often means bringing gold concentration within the linear range of analytical techniques such as atomic absorption spectrometry and atomic emission spectrometry [15–18]. Separation and preconcentration methods such as coprecipitation, solvent extraction, membrane filtration, cloud point extraction, ion exchange, etc. have been used for this purpose.

Solid phase extraction is important in the preconcentration-separation studies for gold ions in environmental samples [19–22] due to its simplicity and ease of adaptation of automatic procedures. Various solid phase extractors such as carbon nanofibres [4], chelating resins [23], Amberlite resins [12,24,25], activated carbon [26], micro-organisms [27], etc. have been used for preconcentration and separation of gold by researchers around the world.

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903428735
http://www.informaworld.com

Carbon nanotubes have good adsorption properties such as a high surface area, hydrophobicity and high adsorption capacities [26–30]. Thus, carbon nanotubes have been used in the solid phase extraction of metal ions, including gold and organic substances at trace levels [9,26–32].

In this work, a preconcentration-separation procedure has been established for gold(III) ions by solid phase extraction on double-walled carbon nanotubes in water and geological samples. The effects of some parameters such as concentration of hydrochloric acid, sample volume and matrix ions, etc. were investigated.

2. Experimental

2.1 *Reagents and solutions*

Analytical reagent-grade chemicals were employed for the preparation of all solutions. The water used in all experiments was purified in a Human Model RO 180, resulting in water with a conductivity of $1\,\mu S\,cm^{-1}$. Stock solutions of Au, $1000\,\mu g\,mL^{-1}$ in 5% HCl were obtained from Sigma and diluted daily to obtaining reference and working solutions. Other stock solutions were prepared by dissolving a suitable salt of each element in a water or acid solution. Standards and model solutions were prepared by dilution of stock solutions prior to use.

Double-walled carbon nanotubes (Aldrich no: 637351-1G) were purchased from Aldrich, Milwaukee, WI, USA. The BET surface area is $>600\,m^2\,g^{-1}$ and the bulk density is $0.12–0.14\,g\,mL^{-1}$. The outer and inner diameter are 5 nm and 1.3–2.0 nm, respectively. The length is 50 μm [33].

2.2 *Instruments*

The instrumental detection system used in this work was a Perkin-Elmer Model 3110 flame atomic absorption spectrometer. The operating parameters for the analysis of gold were those recommended by the manufacturer. Atomic absorption measurements were conducted in an air/acetylene flame. The wavelength, slit and lamb current for determination of the gold were 242.8 nm, 0.7 nm and 10 mA, respectively. All measurements were carried out without background correction. A pH meter, Nel pH-900 Model glass-electrode, was employed for measuring pH values in the aqueous phase.

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of about 10 mm with a suspension of 200 mg of double-walled carbon nanotubes in water. Prior to use, the column was preconditioned with a buffer solution. After each experiment, the column was rinsed with water and stored for the next experiment.

2.3 *Model studies for analyte ions*

The method was investigated with model solutions containing 10–20 μg of Au in 25–30 mL prior to its application to real samples. The model solutions were prepared with $0.1\,mol\,L^{-1}$ HCl. It was loaded to the top of the prepared column and percolated using a water aspirator vacuum at a $1.0\,mL\,min^{-1}$ rate. Then, the column was washed with the solution used for preparation of the model solution. Gold(III) was eluted with 8–10 mL of $1\,mol\,L^{-1}$ HNO_3 in acetone at a $1.0\,mL\,min^{-1}$ rate. The effluent was evaporated to 1–2 mL, and then cooled. Acetone was completely evaporated at this stage. It was transferred to a volumetric flask and made up to 10 mL with distilled water. Gold in this solution was determined by flame atomic absorption spectrometry.

2.4 *Applications*

The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. Prior to analysis the concentration of HCl in the sample was adjusted to 1.0 mol L^{-1}. Then the preconcentration-separation procedure given above was applied to the final solutions.

The anode slime and geological samples were dried at 110°C for two hours. Then, 200 mg for anode slime or 1.0 g of geological sample was decomposed with 10 mL of aqua regia and the solution was evaporated to dryness and the process was repeated two times. An amount of 10–15 mL of a solution containing 0.1 mol L^{-1} HCl was added to the residue. The mixture was filtered through a filter paper, and the insoluble part was washed with the mixture of 0.1 mol L^{-1} HCl. The filtrate and washings that were 30 mL in the receiving vessel were passed through the column and then gold was determined as described above.

3. Results and discussions

3.1 *Influences of hydrochloric acid concentration*

Gold(III) ions are known to exist as $[AuCl_4]^-$, $[AuCl_3OH]^-$ and $[AuCl_2(OH)_2]^-$ anions in chloride media [34,35]. These complexes were adsorbed on the solid phases with the physical interaction of the surface of adsorbents and complexes [34,36,37]. This phenomenon is the main point of the work that is presented here. The influences of hydrochloric acid on the retentions of gold as chloro complexes were investigated in the concentration range of 0.05–1.0 mol L^{-1}. The results are depicted in Figure 1. Gold(III) was quantitatively recovered in the acid concentration range of 0.05–0.5 mol L^{-1}. Higher than 0.5 mol L^{-1}, the recoveries of Au(III) were not quantitative. All further work was carried out at 0.1 mol L^{-1} HCl concentration.

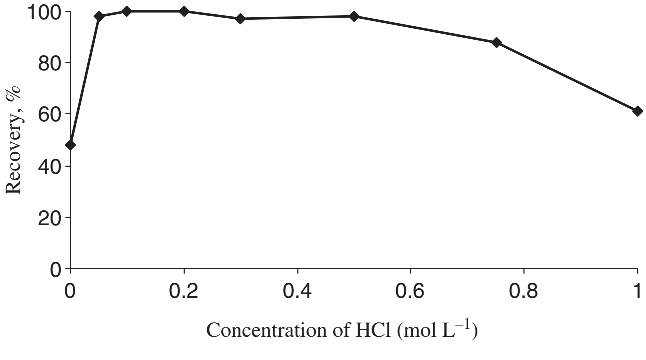

Figure 1. The effect of HCl concentration on the recoveries of Au(III) on double-walled carbon nanotubes ($N = 3$; Eluent: 1 mol L^{-1} HNO_3 in acetone).

3.2 *Effect of eluent type*

To desorp adsorbed gold(III) from nanotubes, various eluting solutions given in Table 1 were examined with regard to the optimal working conditions with model solutions. Quantitative recoveries were obtained with 1.0 mol L^{-1} HCl in acetone, 1.0 mol L^{-1} HNO_3 in acetone, 2.0 mol L^{-1} HNO_3 in acetone, 2.5 mol L^{-1} HNO_3 in acetone and 3.0 mol L^{-1} HNO_3 in acetone. These solutions were effective to break to interactions between chloro complexes-nanotubes. An amount of 1.0 mol L^{-1} HNO_3 in acetone was selected as an eleunt for further studies. The effect of the eluent volume was also studied. Quantitative recovery values were obtained for gold(III), both 5 and 10 mL of eluent volume.

3.3 *Effect of sample volume*

To improve preconcentration factors on the solid phase extraction [37–42], the volume of sample solution is a main factor. The influences of sample volume on the recoveries were investigated by using model solutions. The results are depicted in Figure 2. Gold(III) ions were quantitatively recovered in the sample volume range of 25–750 mL. The preconcentration factor is calculated by the ratio of the highest sample volume (750 mL) and the lowest final volume (5 mL). The preconcentration factor was 150.

The enrichment factors calculated as the ratio of the slope of the calibration graph with and without preconcentration was 77 for gold(III) ion. The consumptive index (CI) is defined as the sample volume (millilitres), consumed to reach a unit of enrichment factor (EF): CI = Vs (mL)/EF, where Vs is the sample volume. CI was calculated as 9.74.

3.4 *Flow rates for sample and eluent*

The influences of flow rates of sample and eluent solutions on the recoveries of gold(III) from carbon nanotubes were investigated. Quantitative recoveries of gold(III) were obtained up to 2.0 mL min^{-1} of flow rates of sample and eluent solutions. All further work was carried out at 1.0 mL min^{-1} of flow rates of sample and eluent solutions.

Table 1. Effects of some eleuting solutions on the desorption of gold(III) from carbon nanotubes ($N = 3$).

Eluent type	Recovery of gold (%)
1.0 mol L^{-1} HNO_3	20 ± 2
2.0 mol L^{-1} HNO_3	33 ± 1
1.0 mol L^{-1} HCl	17 ± 3
2.0 mol L^{-1} HCl	30 ± 2
1.0 mol L^{-1} NH_3	18 ± 2
2.0 mol L^{-1} NH_3	25 ± 3
1.0 mol L^{-1} HCl in acetone	96 ± 2
0.5 mol L^{-1} HNO_3 in acetone	50 ± 1
1.0 mol L^{-1} HNO_3 in acetone	98 ± 1
2.0 mol L^{-1} HNO_3 in acetone	97 ± 2
2.5 mol L^{-1} HNO_3 in acetone	99 ± 1
3.0 mol L^{-1} HNO_3 in acetone	100 ± 0

3.5 *Interferences*

In order to solve the interference effects of the matrix components of real samples in atomic absorption spectrometric determinations, solid phase extraction procedures have been preferred by the researchers [43–57]. The effect of foreign ions on the determinations of gold(III) with the proposed preconcentration procedure were examined by using test solutions containing gold(III). The results are summarised in Table 2. No interference was found from alkaline, alkaline earth and transition metal ions over the investigated concentration range. Also, there was no interference in presence of sulphate, chloride, and nitrate ions at high concentrations.

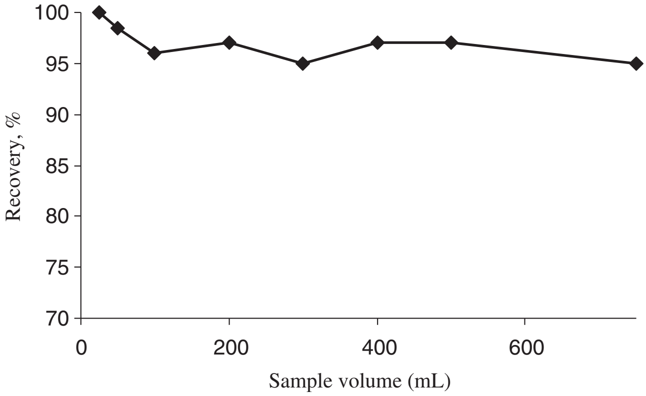

Figure 2. The influences of sample volume on the recoveries of gold(III) ($N = 3$).

Table 2. Influences of matrix ions on the recoveries of gold(III) ($N = 3$, eluent: $1\,\mathrm{mol\,L^{-1}}$ HNO_3 in acetone).

Ion	Concentration ($\mathrm{mg\,L^{-1}}$)	Added As	Recovery of gold (%)
Na^+	20000	NaCl	99 ± 1
K^+	5000	KCl	96 ± 1
Mg^{2+}	5000	$Mg(NO_3)_2$	95 ± 1
Ca^{2+}	3000	$CaCl_2$	97 ± 1
Cu^{2+}	20	$Cu(NO_3)_2 \cdot 3H_2O$	99 ± 2
Mn^{2+}	20	$MnSO_4 \cdot H_2O$	96 ± 1
Fe^{2+}	20	Metallic Fe	95 ± 1
Co^{2+}	20	$Co(NO_3)_2 \cdot 6H_2O$	99 ± 1
Pb^{2+}	20	$Pb(NO_3)_2$	95 ± 1
Ni^{2+}	20	$Ni(NO_3)_2 \cdot 6H_2O$	96 ± 1
Cd^{2+}	15	$Cd(NO_3)_2 \cdot 4H_2O$	97 ± 1
Zn^{2+}	15	Metallic Zn	95 ± 1
Cl^-	10000	NH_4Cl	99 ± 2
SO_4^{2-}	5000	Na_2SO_4	96 ± 1
NO_3^-	5000	KNO_3	97 ± 1

Table 3. Test of addition/recovery for the application of presented method ($N = 6$).

	Tap water		Beypazari mineral water		Synthetic sea water	
Added ($\mu g\, g^{-1}$)	Found ($\mu g\, g^{-1}$)	Recovery (%)	Found ($\mu g\, g^{-1}$)	Recovery (%)	Found ($\mu g\, g^{-1}$)	Recovery (%)
0	0	–	0	–	0	–
2.5	2.5 ± 0.1	100 ± 1	2.45 ± 0.30	98 ± 1	2.4 ± 0.1	96 ± 2
5.0	4.85 ± 0.20	97 ± 1	4.85 ± 0.25	97 ± 2	5.0 ± 0.0	100 ± 0
10.0	10.0 ± 0.1	100 ± 0	10.0 ± 0.1	100 ± 0	9.7 ± 0.3	97 ± 1
20.0	19.6 ± 0.3	98 ± 2	19.4 ± 0.4	97 ± 1	19.6 ± 0.3	98 ± 1

Table 4. Application of presented method to geological samples from different sites of Turkey (Sample amount: 1.0 g, Eluent: 1.0 mol L^{-1} HNO_3 in acetone, Eluent volume: 5 mL, $N = 5$).

	Chromium mine from Alacakaya, Elazig –Turkey		Gold mine from Sart, Salihli Manisa –Turkey		Soil from Goreme Nevşehir –Turkey	
Added ($\mu g\, g^{-1}$)	Found ($\mu g\, g^{-1}$)	Recovery (%)	Found ($\mu g\, g^{-1}$)	Recovery (%)	Found ($\mu g\, g^{-1}$)	Recovery (%)
0	5.98 ± 0.09	–	39.30 ± 1.20	–	0	–
5.0	10.76 ± 0.29	96 ± 2	44.20 ± 0.70	98 ± 2	4.90 ± 0.10	98 ± 1
10.0	15.90 ± 0.40	99 ± 1	48.90 ± 1.10	96 ± 2	9.70 ± 0.20	97 ± 2
20.0	25.70 ± 0.70	95 ± 2	58.10 ± 1.30	94 ± 2	19.20 ± 0.70	96 ± 2

3.6 *Analytical performance*

The accuracy of the results for the procedure presented here was verified by analysing the concentration after addition of known amounts of gold(III) ions into a 250 mL of tap, mineral water and synthetic sea water sample [58]. The results are given in Table 3. Good agreement was obtained between the recoveries of analyte for spiked and control samples using the experimental procedure for the gold(III) ions. The detection limits of gold(III) ions based on three times the standard deviations of the blank ($k = 3$, $N = 10$) in a sample volume of 750 mL was 1.5 $\mu g\, L^{-1}$.

To examine, the adsorption capacity of carbon nanotubes, a batch method was selected. To 0.1 g carbon nanotubes was added 50 mL of solution containing 1.0 mg of gold(III) at pH 6.0. After shaking, the mixture was filtered. An amount of 10 mL of the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. The capacity of sorbent was found as 10.0 mg g^{-1} for gold(III).

3.7 *Applications to real samples*

The application of the method presented here was performed for the determination of gold content of geological samples from different sites of Turkey and three anodic slime samples. The results are given in Table 4 for geological samples and in Table 5 for anodic slime samples.

Table 5. Gold levels of three anodic slime samples after application of the presented separation-preconcentration method (Eluent: 1.0 mol L^{-1} HNO_3 in acetone, Eluent volume: 5 mL, $N = 5$).

Sample	Amount of sample (mg)	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)
Birtek Metal Kaplama	100	0	192 ± 19
Birtek Metal Kaplama	200	0	186 ± 17
Birtek Metal Kaplama	100	20	213 ± 15
HES	100	0	958 ± 19
ELBAK	100	0	1677 ± 23

4. Conclusion

A simple separation-preconcentration procedure for the flame atomic absorption spectrometric determination of gold by solid phase extraction on double-walled carbon nanotubes in geological and anodic slime samples has been established. Accurate and precise results were obtained without any interference effects of the matrix components of the samples.

Acknowledgements

The authors are grateful for the financial support of the Unit of the Scientific Research Project of Erciyes University (Project No: FBY-09-961).

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