

New amino acid modified silica gel sorbents for solid phase extraction of Au (III)

P. Petrova^{1*}, I. Karadjova², M. Chochkova¹, I. Dakova², M. Karadjov³

¹ South-West University "Neofit Rilski", Faculty of Mathematics and Natural Sciences, Department of Chemistry, 66, Ivan Mihailov Str, 2700, Blagoevgrad, Bulgaria

² Sofia University, "St. Kliment Ohridski", Faculty of chemistry and pharmacy, 1, blv. J. Boucher, 1164 Sofia, Bulgaria

³ Geological Institute, Bulgarian Academy of Science, Acad. G. Bonchev Str. bl.24, 1113 Sofia, Bulgaria

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Two new sorbents, silica gel modified with Cystine (Sig-Cys-S-S-Cys) and silica gel modified with *N*-Benzyloxycarbonyl-*L*-Methionine (Sig-Z-Met-OH) were prepared and examined for quantitative extraction of Au (III) from hydrochloric acid solutions. Several parameters affecting the sorption efficiency such as pH of the sample solution, sorption time, eluent type and volume were optimised in order to achieve quantitative extraction of Au (III). Experiments performed showed that under optimized conditions the degree of Au (III) sorption does not exceed 43 % by using Sig-Cys-S-S-Cys whereas Sig-Z-Met-OH enables fast and quantitative retention of Au (III) from 0.1-0.01 mol L⁻¹ HCl and could be used for the separation and preconcentration of Au (III). The analytical procedure was developed for the determination of Au in gold containing cosmetics based on two steps: solid phase extraction of Au (III) and measurement of extracted Au by ICP-OES. The limit of detection achieved is 0.1 µg g⁻¹ Au in the face cream and the relative standard deviation varied in the range 6-11% for the concentration range 0.1-1 µg g⁻¹ Au in the face cream. The accuracy of the developed analytical procedure was verified by direct analysis using ICP-MS.

Keywords: solid phase extraction, noble metals, atomic spectrometry

INTRODUCTION

Platinum group elements (PGEs) and gold are distributed at very low concentration in the earth crust. The typical concentration of gold in ore is in the range of 5-30 g/t [1]. However, their application in electrical and electronic industries, in medicine and in jewelry leads to their spread in the environment where significant quantities of noble metals are converted into bioavailable forms, mainly as chloro or organic complexes [2-5]. Despite the elevated anthropogenic PGEs levels, their concentration remains quite low for direct instrumental determination and usually analytical procedure which includes preliminary separation and concentration of analytes has to be used [6]. As a rule reliable results could be obtained after careful optimization of the parameters of analytical method which combines the application of sensitive analytical techniques such as ICP-MS, ICP-OES or ETAAS with suitable enrichment procedure. Solid phase extraction technique using different kind of solid sorbents ensures high enrichment factor, rapid phase separation and the ability of combination with different detection techniques [7]. Silica gel has been widely used as a sorbent or as a support due to its good mechanical and chemical properties, high porosity, large surface, resistance to

swelling, as well as high thermal stability. The extraction efficiency and selectivity of silica gel has been improved by its physical and chemical modification with various chemical reagents, in this way suitable functional groups have been chemically or physically bonded to the reactive sites on the silica surface. Chelating agents with *N*- and *S*- containing groups are highly efficient for the selective sorption of noble metals and could be used for physical modification of silica gel [8, 9]. In the presence of HCl noble metals' chlorocomplexes could form stable ion associates with protonated nitrogen-containing reagent and quantitatively retained on the surface of silica gel [9, 10].

The immobilization of chitosan and amino acids such as glycine, valine, leucine, serine and lysine has been already used as an approach for preconcentration of Au (III), Pt (IV) and Pd (II) [12-14]. Recently *Hastuti et al.* [15] used *L*-arginine functionalized silica gel as an effective adsorbent for gold (III), *Mladenova et al.* prepared and studied sorbent based on cysteine modified silica gel for preconcentration and separation of noble metals Au (III), Pd (II), Pt (II), Pt (IV) [16].

The aim of the present work is to prepare silica gel sorbents physically modified with sulfur containing amino acids *Z*-Methionine (*N*-Benzyloxycarbonyl-Methionine) and Cystine (unmodified), and to investigate their sorption efficiency towards Au (III). Additionally our interest is to examine the reliability of physical

* To whom all correspondence should be sent:
E-mail: petya_dukova@yahoo.com

functionalization of silica particles and to check out if the simplified preparation technique provides satisfactory results. Analytical application of sorbents prepared for Au determination in cosmetics is presented.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade and were used without further purification. The stock standard solution for Au (III) (1000 mg L⁻¹) was Sigma–Aldrich (Germany) in 5% HCl. Working standard solutions for Au were prepared daily by appropriate dilution of the stock standard solution. Silica gel for column chromatography ≤0.063 mm, ≥230 mesh ASTM, the amino acids cystine and *L*-methionine and *N*-(Benzyloxycarbonyloxy) succinimide were purchased from Sigma-Aldrich Ltd. Analytical grade sodium bicarbonate (NaHCO₃, Sigma-Aldrich, Germany), acetone (CH₃COCH₃, Sigma-Aldrich, Germany), ethyl acetate (CH₃COOC₂H₅, 99.8%, Sigma-Aldrich, Germany) and sodium sulfate (Na₂SO₄, Merck, Germany) were used for synthesis of *N*-Benzyloxycarbonyl-*L*-methionine. HCl (37%), HNO₃ (68%) and NH₃ (25%) were purchased from Merck, Germany.

Apparatus

FAAS measurements were carried out on a Perkin- Elmer AAnalyst 400 spectrometer, with air/acetylene flame under optimal instrumental parameters, ensuring maximal signal to noise ratio. The light source was hollow cathode lamps for Au. The spectral bandpass and wavelengths used were as recommended by the manufacturer. The wavelength used for Au AAS measurement is 242.8 nm. ICP-OES measurements were performed on an ICP-OES spectrometer Ultima 2, Jobin Yvon under optimized instrumental parameters using wavelength 242.795 nm.

A Milestone Ethos 900-Mega II microwave oven with a PTFE-vessel rotor was employed for samples digestion.

The centrifuge K-1000 (KUBOTA Corporation, Osaka, Japan) was used for the centrifugation of modified silica sorbent in batch experiments.

Synthesis of N-Benzyloxycarbonyl-L-methionine (Z-Met-OH) [17]

The suspension of *L*-methionine (1.5 g, 10 mmol) in deionized water (20 mL) was prepared and mixed with NaHCO₃ (0.84 g, 10 mmol) and 25 mL acetone. Then *N*-(Benzyloxycarbonyloxy) succinimide (2.5 g, 10

mmol) was added and the reaction mixture was stirred at room temperature overnight. After evaporation of the acetone *in vacuo*, the aqueous layer was acidified with 1 mol L⁻¹ HCl to pH 2.5 and extracted with ethylacetate (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and evaporated *in vacuo*. Yield (65%); mp 67-69°C.

Preparation of modified silica gels: silica gel modified with Z-methionine and silica gel modified with cystine

The silica gel modified with Z-Methionine (Sig-Z-Met-OH) and silica gel modified with Cystine (Sig-Cys-S-S-Cys) were prepared following the procedure described by *Bartyzel et al.* [18] and further optimized by Petrova et al. [19].

The commercially available silica gel was activated by refluxing with concentrated HCl for 4 h, because the commercial silica gel possesses a low concentration of suitable surface silanol groups, required for further modification. Thereafter it was filtered, washed with deionized water until the filtrate was neutral and dried in an oven at 150 °C for 12 h to remove surface adsorbed water. The activated silica gel was refluxed separately with the modifiers Z-methionine or cystine in ratio 9:1 w/w in an acetone media for 8 h. Finally the mixture was vigorously stirred at room temperature to complete the solvent evaporation and then dried at 40°C for 1 h.

Sorption/desorption studies

Aqueous standard solution (10 mL) containing Au (10 mg L⁻¹) was mixed with 50 mg of the sorbent in the presence of various concentrations of HCl. The mixture was shaken for 10-40 min with an electric shaker and then centrifuged. In order to investigate the degree of sorption supernatant solution was removed and analyzed by FAAS as effluante. The sorbent was washed with deionized water and Au was eluted from the sorbent particles with different eluate solutions. In order to investigate the degree of elution, metal ion content in eluate was determined by FAAS after sorbent centrifugation. The degree of sorption, D%, and elution, R% is calculated using the following equations:

$$D\% = [(C_{\text{initial}} - C_{\text{effluante}})/C_{\text{initial}}] \times 100,$$

$$R\% = [(C_{\text{initial}} - C_{\text{effluante}})/C_{\text{eluate}}] \times 100,$$

where C_{initial} is the initial amount of Au, $C_{\text{effluante}}$ is the amount of Au measured in the supernatant (effluante solution) and C_{eluate} is the amount of Au measured in the eluate solution.

Determination of Au in cream samples

Digestion of cream samples: All plastic and glassware were soaked in 5% HNO₃ solution for 24 h and rinsed with deionized water before use.

The cream sample was dried in an oven at 105 °C to constant weight and then stored in desiccator. About 0.3 g of the dried sample was directly weighed into PTFE digestion vessel. Then 10.0 mL HCl (37%) and 3.5 mL HNO₃ (68%) were added and the mixture was left at room temperature for 24 h. The MW digestion programme was as follows: 10 min at 250 W; 5 min at 400 W; 5 min at 500 W; 5 min at 600 W. After cooling, the solution was quantitatively transferred in a volumetric flask and diluted up to 25 mL with 0.02 mol L⁻¹ HCl [20].

Determination of Au: 20 mL of above prepared solution of digested cream sample were transferred in a centrifuge tube, 50 mg sorbent was added and mixture was shaken for 30 min. After centrifugation the sorbent was washed with deionized water and eluted with 1 mL 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl. The concentration of Au in an eluate obtained was measured by ICP-OES.

RESULTS AND DISCUSSION

Optimization of the experimental conditions for SPE of Au (III)

Influence of pH on Au (III) sorption

The pH of the solution is an important factor influencing the degree of sorption because it affects the protonation of the functional groups on the sorbent surface and also defines the chemistry of Au ions.

The effect of the HCl molarity on Au (III) adsorption was investigated in batch mode for the two studied sorbents by varying the HCl concentration in the range 0.01 - 2.7 mol L⁻¹, applying the procedure described in section 2.5. The results obtained are presented in Table 1.

The quantitative sorption of Au (III) on Sig-Z-Met-OH was achieved at HCl concentration in the

range 0.1-0.01 mol L⁻¹ reaching 96-98%. The high degree of Au (III) sorption on Sig-Z-Met-OH in the presence of HCl might be explained with the fact that Au (III) forms anionic chlorocomplexes [AuCl₄]⁻ whereas amino- and S-methyl thioether groups on the sorbent surface are protonated and thus charged positively [13,14,21,22,23]. Therefore, the Au (III) adsorption is due to the strong electrostatic attraction between the positively charged adsorbent surface and negatively charged chloride complex of Au [15,24].

The two sorbents differ remarkably in their extraction efficiency toward Au (III). Theoretically more considerable sorption capacity is expected for Sig-Cys-S-S-Cys due to the presence of two amino groups and two S atoms in the cystine molecule ([HOOC(NH₂)CHCH₂S-]₂) in comparison with Sig-Z-Met-OH (Z-NH-CH(CH₂CH₂SCH₃)-COOH), with one amino group and one S atom per mol amino acid. However it is obvious that Sig-Cys-S-S-Cys does not ensure satisfactory extraction (less than 44 % for all HCl molarities studied) of Au (III), whereas the sorption on Sig-Z-Met-OH is higher in the whole acidity range. One probable explanation for this observation could be very slow kinetics of sorption on the surface of Sig-Cys-S-S-Cys, as it was mentioned in the literature [23].

Another reason could be the formation of large ion associates which cannot be quantitatively sorbed on the surface of this material as discussed by A. Dubenskiy et al. [25]. Due to the low sorption activity or slow kinetics of sorption process on the surface of Sig-Cys-S-S-Cys, further studies were performed only with Sig-Z-Met-OH sorbent.

Influence of contact time

The kinetics of the Au (III) sorption was investigated in a batch system following the procedure described in section 2.5. It was found that the quantitative sorption was reached within 30 min, which is sufficiently fast for practical applications. The effect of contact time on the Au (III) ions adsorption is presented in Fig. 1.

Table 1. Degree of sorption of Au (III) on Sig-Z-Met-OH and Sig-Cys-S-S-Cys. Data represent an average of three independent experiments

Sorbent	Degree of sorption, %				
	0.01 mol L ⁻¹ HCl	0.1 mol L ⁻¹ HCl	1 mol L ⁻¹ HCl	2 mol L ⁻¹ HCl	2.7 mol L ⁻¹ HCl
Sig-Z-Met-OH	96±3	98±5	92±3	85±4	80±5
Sig-H-Cys-Cys-OH	18±4	18±3	42±4	10±3	4±5

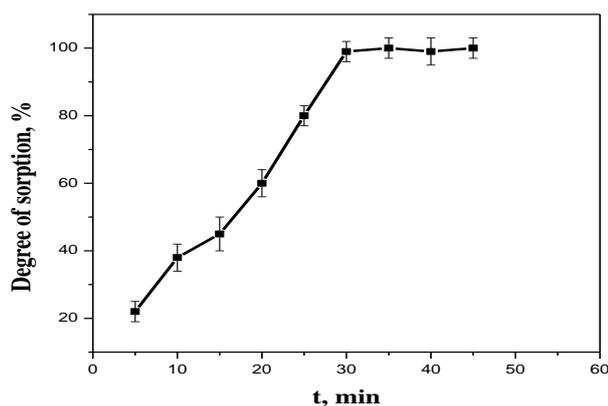


Fig. 1. Adsorption kinetic curves for the Sig-Z-Met-OH ($m_{\text{sorbent}} = 50$ mg, $V = 10$ mL, $C_{\text{Au (III)}} = 10$ mg L⁻¹). Data represent an average of three independent experiments.

Selection of appropriate eluent for Au (III) desorption

Very important factors affecting the extraction efficiency of particular sorbent are the type, volume and concentration of the eluent used for quantitative removal of sorbed metal ions. A series of eluents, presented in Table 2 were tested in order to find the most suitable eluent for desorption of Au(III).

The summarized results (Table 2) showed that the highest recovery was achieved by using 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl as an eluent.

By varying the eluent volume (from 1 to 10 mL) it was found that the optimal volume for full desorption of Au (III) was 1 mL.

ANALYTICAL APPLICATION

The prepared Sig-Z-Met-OH sorbent was examined under optimized chemical parameters for SPE of Au (III) from cosmetics samples, digested using the analytical procedure described in section 2.6. The recovery experiments were performed by spiking cream sample with known amount of Au (III) before MW digestion. Recoveries achieved for spiked cosmetic samples varied between 90 and 103%, confirming the applicability of Sig-Z-Met-OH for Au determination in cosmetic creams (Table 3). Analytical procedure developed permits quantification (LOQ) of 0.1 µg g⁻¹ Au in cosmetic cream sample. Relative standard deviations for the concentration range 0.1–1 µg g⁻¹ Au in cream sample varied between 6–11 % (Table 3).

The procedure was applied for the determination of Au (III) in gold-containing face cream, purchased from the market. The sample was digested according to the procedure described in section 2.6 and the developed SPE-ICP-OES method was used for Au quantification. Further, the results obtained by the proposed method were compared with direct Au determination in the same face cream. Results (0.62±0.07) µg g⁻¹ obtained by SPE-ICP-OES and (0.68±0.06) µg g⁻¹ obtained by direct ICP-MS (performed in external lab) determination agreed very well (Student t-test, 95% confidence limit) thus demonstrating that there are no statistically significant differences between the results obtained by the two methods and confirming the accuracy of developed SPE-ICP-OES method for Au determination in cosmetic creams.

Table 2. Effect of eluent type and concentration on the desorption of gold ions

Eluent	R,%
0.5 mol L ⁻¹ NaClO ₄ and 0.5 mol L ⁻¹ thiourea in 1 mol L ⁻¹ HCl	67±5
0.7 mol L ⁻¹ thiourea in 2 mol L ⁻¹ HCl	98±2
0.1 mol L ⁻¹ thiourea in 1 mol L ⁻¹ HCl	70±5
0.5 mol L ⁻¹ NaClO ₄ in 0.1 mol L ⁻¹ HCl	32±6
96 % ethanol	25±7
0.01 mol L ⁻¹ EDTA in methanol	30±6

Table 3. Analytical figures of merit for the developed SPE-ICP-OES method for Au determination in cosmetic creams (three parallel determinations).

Added, $\mu\text{g g}^{-1}$	Found, (mean \pm sd) $\mu\text{g g}^{-1}$	RSD, %	Recovery, %
0.20	0.18 \pm 0.03	11	90
0.50	0.51 \pm 0.04	8	102
1.0	1.03 \pm 0.06	6	103

CONCLUSION

Two new sorbents Sig-Cys-S-S-Cys and Sig-Z-Met-OH were prepared by simple non-covalently amino acid bonding on the silica surface and were examined for SPE of Au (III). The influence of various important factors such as pH, contact time, eluent type, concentration and volume were studied and Au (III) sorption mechanism was proposed. The experiments demonstrated that the quantitative Au (III) sorption is achieved with Sig-Z-Met-OH in 0.1 mol L⁻¹ HCl reaching degree of sorption 98 \pm 2 %. The developed, optimized solid phase extraction procedure combined with ICP-OES measurements is applied for the determination of Au in gold-containing cosmetics. The accuracy of proposed analytical method was verified by parallel direct analysis with ICP-MS and recovery tests.

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СИЛИКАГЕЛ, МОДИФИЦИРАН С АМИНОКИСЕЛИНИ КАТО СОРБЕНТ ЗА ТВЪРДОФАЗНА ЕКСТРАКЦИЯ НА Au (III)

П. Петрова^{1*}, И. Караджова², М. Чочкова¹, И. Дакова², М. Караджов³

¹ Югозападен университет „Неофит Рилски“, Природо-математически факултет, Катедра по „Химия“, 66, Иван Михайлов, 2700, Благоевград, България

² Софийски университет „Св. Климент Охридски“, Факултет по „Химия и фармация“, 1, бул. Джеймс Баучер, 1164 София, България

³ Българска Академия на Науките, Геоложки Институт, , София 1113, България

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(Резюме)

Синтезирани са два нови сорбента- силикагел, модифициран с цистин (Sig-Cys-S-S-Cys) и силикагел, модифициран с *N*-бензилоксикарбонил-*L*-метионин (Sig-Z-Met-OH). Изследвани са техните сорбционни свойства за количествена екстракция на Au (III) из разтвори на солна киселина. Оптимизирани са няколко параметъра, засягащи сорбционната ефективност, като рН на разтвора, времето за сорбция, вида и обема на елуента, с цел постигане количествена екстракция на Au (III). Показано е, че при оптимални условия степента на сорбция не надхвърля 43%, използвайки сорбента Sig-Cys-S-S-Cys, докато Sig-Z-Met-OH осигурява бърза и количествена сорбция на Au (III) в 0.1-0.01 mol L⁻¹ HCl и може да бъде използван за разделяне и концентриране на Au (III). Предложена е аналитична процедура за определяне на Au (III) в злато-съдържаща козметика, включваща две стъпки: твърдофазна екстракция на Au (III) и определяне на извлечените Au йони с ICP-OES. Постигнатите граници на откриване са 0.1 µg g⁻¹ Au в крем за лице, като относителното стандартно отклонение варира в границите 6-11% за концентрационен интервал 0.1-1 µg g⁻¹ Au в крема за лице. Точността на разработената аналитична процедура е доказана чрез директен анализ с ICP-MS.