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Amino acid functionalized silica gel as a selective sorbent for enrichment of Pt (II)

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In this study we report on the synthesis and applicability of 3 new sorbents based on silica gel impregnated with amino acids or with amino acid derivatives, namely *L*-cystine modified silica gel (SiO_2-Cys-Cys), silica gel modified with *L*-cysteine amide of 4-aminoantypirine (SiO_2–Cys) and silica gel modified with *N*-benzyloxycarbonyl-*L*-methionine (SiO_2-Met) as an efficient sorbent for solid-phase extraction of Pt from hydrochloric acid solutions. Extraction efficiency and selectivity of the sorbents toward Pt(II)/Pt(IV) were studied by batch procedure. The influence of analytical parameters such as acidity of the sample solution, eluent type and volume, effects of foreign ions on the sorption/desorption behavior of Pt(II)/Pt(IV) were investigated. The results obtained demonstrate that SiO_2-Cys and SiO_2-Met showed high sorption activity toward Pt(II) while SiO_2-Cys-Cys is not able to extract quantitatively neither Pt(II) nor Pt(IV). The experiments revealed that the new sorbents SiO_2–Cys and SiO_2-Met are highly selective toward Pt(II) extracted as $Pt(Cl)_4^{2-}$ complex while sorption of Pt(IV) is negligible at the same HCl concentration. Analytical procedure was developed for total Pt determination in cosmetic cream samples, based on solid-phase extraction using SiO_2-Met as an effective sorbent combined with ICP-OES measurements. Under optimised conditions, the limit of quantification achieved for total Pt in cosmetic creams was 0.2 μg g^{-1}, the RSD value varied between 6-16 % for Pt content between 0.2-1 μg g^{-1}. The accuracy of the proposed method was confirmed by the added/found method and by comparative analysis using direct ICP-MS measurements.

Keywords: Solid phase extraction, Noble metal determination, Amino acid modified sorbent

INTRODUCTION

Quantification of Pt in environmental samples is an analytical challenge, even by using highly sensitive ICP-MS spectrometry because of its extremely low environmental concentrations, as well as observed interferences from matrix constituents. In the literature many analytical procedures have been described for noble metals determination in different types of samples, such as road dust [1], airborne particulate matter [2-4], soil [5], sediments [6], water [7,8], biological [9] and geological samples [10]. In most of these procedures an additional separation/enrichment step was included for preliminary Pt enrichment prior to instrumental measurement. Solid-phase extraction is a method frequently utilized for matrix elimination and enrichment of noble metals using various types of sorbents [11], many of them based on silica gel modified with different chelating agents [12-16]. Sorbents based on silica matrix are often applied because of their high mechanical and thermal stability and good chemical resistance in organic solvents and mineral acids. The sorption selectivity is regulated using suitable functional groups fixed on the sorbent surface. Complexing agents containing N- and S- donor groups are employed in enrichment of PGE *via* solid phase extraction [17,18]. Incorporation of chelating functional groups on the support can be accomplished by covalent grafting or by impregnation and physical adsorption of the organic reagent achieved by inclusion in the pores of the support material, by adhesion process or by electrostatic interaction [18,19].

In the present work, we focused our attention on: (i) the synthesis of amino acid derivatives as modifiers for silica gel and preparation of new sorbents for effective separation and enrichment of Pt(II) and (ii) the applicability of the newly synthesized sorbents for the determination of total Pt in cosmetics.

EXPERIMENTAL

Reagents

The stock standard solution for platinum ions (1000 mg L^{-1}) was Sigma–Aldrich (Germany) in 5% HCl. Silica gel for column chromatography ≤0.063 mm, ≥230 mesh ASTM, the amino acids *L*-cisteine, *L*-cystine, *L*-methionine and *N*-(benzyloxycarbonyloxy) succinimide were purchased from Sigma-Aldrich Ltd. Tin (II) chloride ($SnCl_2$) was from Merck, Germany.

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Apparatus

ICP-OES measurements were performed on an ICP-OES spectrometer Ultima 2, Jobin Yvon under optimized instrumental parameters using the wavelength 203.646 nm for Pt II.

A microwave oven Milestone Ethos 900-Mega II was employed for cream sample digestion.

A centrifuge NEYA 8 Giorgio Bormac was used for separation of silica sorbent from the supernatant solutions in the batch experiments.

Synthesis of amino acid derivatives

Synthesis of N-benzyloxycarbonyl-L-methionine: *N*-Benzyloxycarbonyl-*L*-methionine (Z-Met-OH) (Fig. 1) was synthesized according to a previously published method [20].

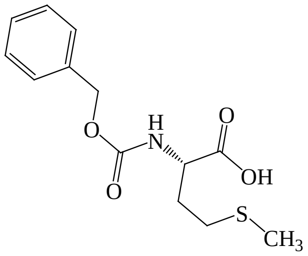

Fig. 1. Structure of *N*-benzyloxycarbonyl-*L*-methionine (Z-Met-OH)

Synthesis of Boc-S-benzyl-L-cysteine amide of 4-aminoantipyrine (Boc-Cys(Bzl)-4-AAP): The synthesis of the target amide Boc-Cys(Bzl)-4-AAP (Fig. 2) was performed according to the EDC/ HOBt method [21].

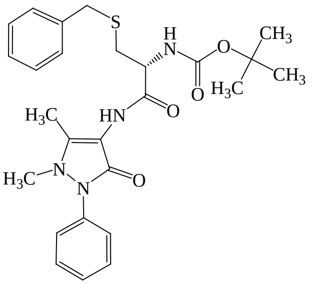

Fig. 2. Structure of Boc-S-benzyl-L-cysteine amide of 4-aminoantipyrine

To a cold solution of Boc-Cys(Bzl)-OH (1.0 g, 3.2 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (0.61 g, 3.2 mmol) and 1-hydroxybenzotriazole (0.43 g, 3.2 mmol) in CH_2Cl_2 (10 ml) was added 4-methylmorpholine (0.35 mL, 3.2 mmol). After 10 min, 4-aminoantipyrine (0.65 g, 3.2 mmol) in 5 ml CH_2Cl_2 was added, and the resultant reaction mixture was stirred for 24 h at room temperature.

The mixture was diluted with CH_2Cl_2 and then washed consequently with 5% $NaHCO_3$ (3 × 30 mL), 10 % Citric acid (3 × 30 ml) and water (3 × 50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by crystallization from hexane-EtOAc to afford 1.1 g (69%) of Boc-Cys(Bzl)-4-AAP amide as pale yellow crystals.

Preparation of modified silica gels: silica gel modified with Z-methionine, silica gel modified with cystine and silica gel modified with Boc-S-benzyl-L-cysteine amide of 4-aminoantipyrine

The physical modification of silica gel with *Z*-methionine-OH (Fig. 1), cysteine amide of 4-aminoantipyrine (Fig. 2) and cystine (Fig. 3.) was performed by the procedure proposed by Bartyzel *et al*. [22] and further optimized by Petrova *et al.* [20].

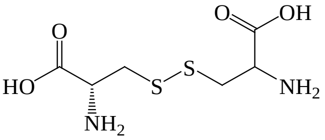

Fig. 3. Structure of the amino acid cystine

Analytical procedures for sorption/desorption studies

To a sample aliquot of 10 ml containing 100 μg Pt(II)/Pt(IV) in HCl, 50 mg sorbent was added. After shaking for 5 – 60 min, the mixture was centrifuged and the supernatant solution was removed and analyzed by ICP-OES as effluate. The sorbent was washed with doubly distilled water and the metal complexes retained on the sorbent were eluted with a solution of thiourea in HCl. In order to investigate the degree of elution, metal ions content in eluate was determined by ICP-OES.

The degree of sorption was calculated using the following equation:

$$S,\% = [(C_i - C_{ef})/C_i] \times 100$$

where S is the degree of sorption (%), C_i is the total cation concentration in the initial solution and C_{ef} is the final concentration of metal ion in the effluate solution after extraction.

The degree of elution from the sorbent was obtained by the equation:

$$E,\% = (C_{el}/C_s) \times 100$$

where C_{el} is the amount of metal ion in the eluate after extraction, C_s is the amount loaded on the sorbent.

Analytical procedure for the determination of Pt in cream samples

Microwave digestion of cream samples: About 0.3 g of the sample was weighed into a closed vessel to prevent the evaporation of the volatile fractions in the cream. Then 10.0 mL of HCl (37%) and 3.5 mL of HNO_3 (68%) were added and the mixture was left at room temperature for 24 h. The MW digestion was conducted using the following program: 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 to a volumetric flask and diluted up to 25 mL with 0.02 mol L^{-1} HCl [23].

Determination of Pt(II): 50 mg SiO_2-Met sorbent and 20 mL solution of digested cream sample to which 1 ml 1 M $SnCl_2$ was added were transferred to a 50 mL centrifuge tube and shaken for 30 min. After centrifugation the sorbent was washed with deionized water and Pt(II) was eluted with 2 mL of thiourea solution in 2 mol L^{-1} HCl. The concentration of Pt(II) in the eluate was measured by ICP-OES.

RESULTS AND DISCUSSION

It is well known that the extraction efficiency of sorbents for noble metals is enhanced by their modification with sulfur-containing compounds [24]. In the present study we chose as modifiers sulfur containing amino acids *L*-cystein, *L*-methionine and *L*-cystin with different S-containing functional groups such as thioether (-SR) and disulfide (-S-S). In order to increase the sorption ability, we furthermore additionally functionalized some of the amino acids introducing one more chelating group. After the synthesis of the amino acid derivatives they were impregnated on the silica gel by physical adsorption and further investigated as efficient sorbents for Pt.

Optimization of the experimental conditions for solid phase extraction (SPE) of Pt (II)

Influence of HCl concentration: The protonation/deprotonation of N- and S- containing functional groups which is related to their pKa, strongly depends on the pH of the solution. On the other hand, in HCl media noble metals form anionic chloro complexes which compositions and charges vary with the HCl concentration. Consequently, the degree of Pt sorption on amino acid modified silica gel sorbent should be strongly influenced simultaneously by pH value and HCl concentration in the sample solution, hence sorption experiments for optimization of the hydrochloric acid concentration were performed.

The results obtained for the degree of sorption of Pt(II) and Pt(IV) in 0.01 - 3 mol L^{-1} HCl for the newly synthesized sorbents in presence and absence of $SnC1_2$ as a reducing agent are shown in Table 1.

The silica gel sorbents containing cysteine and methionine as modifiers, SiO_2-Cys and SiO_2-Met, ensured high degree of sorption between 93-95% in the presence of 0.1-1 mol L^{-1} HCl for Pt(II) and Pt(IV) after reduction with $SnCl_2$, whereas the degree of sorption for SiO_2-Cys-Cys was less than 20 % for the same HCl concentration for both Pt species.

It can be concluded that SiO_2-Cys and SiO_2-Met ensured very good separation of Pt(II) from Pt(IV) at low HCl concentration around 0.1 mol L^{-1}, which might be used for their selective determination. Total Pt in the sample should be determined in the presence of $SnCl_2$ as reducing agent for Pt(IV).

The electrostatic attraction between anionic chlorocomplexes $[PtCl_4]^{2-}$ and positively charged amino- and S- thioether groups on the sorbent surface is one of the possible reasons for the quantitative Pt(II) sorption in HCl media. Complex formation is another possible mechanism of Pt binding on the amino acids derivatives as it was confirmed by V. Joshi [25] who found that the amino acids *L*-cysteine and *DL*-homocysteine behave as bidentate ligands, bonded to Pt(II) *via* ionized sulfur and amino nitrogen while carboxylate groups remain un-coordinated and protonated. However, although SiO_2-Cys-Cys contains an S-group it does not ensure satisfactory extraction which may be attributed to a difference in disulfide (-S-S-) moieties chelating properties or to some steric, geometrical or kinetic factors. The most probable explanation for the low extraction efficiency of SiO_2-Cys and SiO_2-Met toward Pt(IV) is the fact that Pt(IV) complexes in an octahedral geometry are said to be substitution-inert.

Table 1. Influence of HCl concentration on the degree of sorption of Pt(II) and Pt(IV). Data represent an average of three independent experiments.

Sorbent	Metal ion	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	3 mol L^{-1} HCl
SiO_2-Met	Pt(II)	85±6	94±3	96±4	85±7	87±5
	Pt(IV)	< 1	< 1	35±4	40±8	38±9
	Pt(IV)/$SnC1_2$	87±8	94±7	95±6	87±6	86±4
SiO_2-Cys	Pt(II)	86±3	91±5	94±5	90±4	95±6
	Pt(IV)	< 1	<1	23±4	33±4	35±4
	Pt(IV)/$SnC1_2$	88±6	90±7	93±4	92±5	94±6
SiO_2-Cys-Cys	Pt(II)	14±4	18±6	19±6	11±4	3±1
	Pt(IV)	<1	<1	<1	3±1	2±1
	Pt(IV)/$SnC1_2$	11±4	20±7	15±2	10±4	2±1

Summarizing the results obtained for Pt(II), acidity in the range 0.5 - 1 mol L^{-1} HCl was accepted as optimal for quantitative and selective sorption of Pt(II). Total Pt content can be found under the same acidity range after reduction of Pt(IV) with $SnCl_2$ using both sorbents SiO_2-Cys and SiO_2-Met.

The optimization procedure was further continued by carrying out Pt(II) desorption experiments with different types of eluents. Results obtained revealed that 0.7 mol L^{-1} thiourea in 2 mol L^{-1} HCl is the optimal eluent ensuring fast and quantitative elution of Pt(II) sorbed on both SiO_2-Cys and SiO_2-Met. The effect of the eluent volume on the metal desorption was investigated in the range of 1–5 mL. The complete Pt(II) desorption was reached with 2 ml of 0.7 mol L^{-1} thiourea in 2 mol L^{-1} HCl.

Kinetic studies

Kinetic characteristics of the sorption/ desorption process are very important features for sorbents practical application and are connected with their nature and surface properties. Sorbents based on impregnated silica gel are usually characterized by good kinetic properties ensured by the large surface area and easy accessibility of the functional groups [26]. In our study the time for establishing the sorption equilibrium for the investigated sorbents was varied from a few minutes to one hour. The kinetics of the sorption process of Pt(II) was examined in a batch system with 50 mg of SiO_2-Cys and SiO_2-Met particles in 1 mol L^{-1} HCl for 5–60 min. The kinetics of desorption was studied for both sorbents, for the same time interval using the optimal eluent. Results revealed quantitative Pt(II) sorption on SiO_2-Cys and SiO_2-Met within 30 min, and quantitative desorption with the optimal eluent for 15 min.

Selectivity of the sorbents

The selectivity of the newly synthesized sorbents towards Pt(II) was tested using model solutions containing Pt(II) and non-noble metals in a batch mode under optimized chemical conditions for sorption. The results presented in Table 2 show that at optimal HCl concentration the degree of sorption for the non-noble cations is almost negligible, demonstrating high selectivity of the SiO_2-Cys and SiO_2-Met sorbents towards Pt(II).

Analytical application

Recovery experiments were performed to assess the applicability of the SiO_2-Met sorbent for separation and concentration of Pt(II) in real samples. Our attention was turned to the cosmetic samples where Pt is recently being added as the newest ingredient in anti-aging creams. A cream sample (without Pt) was mineralized using MW digestion procedure and known amounts of Pt(IV) were added before mineralization.

Table 2. Matrix interferences of some metal ions on the recovery of Pt(II) by SPE using SiO_2-Met and SiO_2-Cys sorbents (10 mL sample solution, 1 mol L^{-1} HCl, 30 min sorption time; three parallel determinations).

Metal ions	Added (mg L^{-1})	Recovery, %	
		SiO_2-Cys	SiO_2-Met
Al (III)	1000	< 1	< 1
Zn (II)	1000	< 1	< 1
Ni (II)	1000	<1	< 1
Mn (II)	1000	<1	< 1
Cu (II)	2000	<1	< 1
Fe (III)	1000	<1	< 1
Pt(II)	50	94.0 ± 5	94.9 ± 4

After digestion $SnCl_2$ was added to the sample solution and stirred with 50 mg SiO_2-Met for 30 min. After centrifugation the sorbent was washed with distilled water and the retained Pt was eluted with 2 mL of 0.7 mol L^{-1} thiourea in 2 mol L^{-1} HCl and measured by ICP-OES. Recoveries for the investigated element in spiked cream samples varied in the range 93–104 % demonstrating the applicability of the proposed analytical procedure (Table 3).

Table 3. Recovery studies for the determination of Pt(II) by SPE and ICP-OES measurements, using SiO_2-Met (20 mL sample solution, 1 mol L^{-1} HCl, 30 minutes sorption time; three parallel determinations).

Added, μg g^{-1}	Found, (mean±sd) μg g^{-1}	RSD, %	Recovery, %
0	BDL*	-	-
0.2	0.19±0.03	16	93
0.5	0.51±0.04	8	103
1.0	1.02±0.06	6	104

*BDL – below detection limits

The reached limits of quantification (LOQ), calculated as ten time the standard deviation of the blank, are 0.2 μg g^{-1} Pt in the cosmetic cream sample. Relative standard deviations for the concentration range 0.2–1.0 μg g^{-1} Pt in the cream sample varied between 6-16 % (Table 3).

The developed SPE-ICP-OES procedure was applied for the determination of Pt in Pt-containing cream, purchased from the market and the results were compared with those obtained by direct ICP-MS measurements of the same sample after MW digestion.

Results (0.25 ±0.05) μg g^{-1} found by SPE-ICP-OES and (0.21±0.05) μg g^{-1} found by direct ICP-MS (performed in an external lab) agreed very well

(Student’s 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 the developed SPE-ICP-OES method for Pt determination in cosmetic creams.

CONCLUSION

Sorbents SiO_2-Met and SiO_2-Cys based on newly synthesized derivatives of cysteine and methionine, respectively, impregnated on silica gel surface were prepared and studied for the separation and enrichment of Pt. The chemical conditions for quantitative sorption of Pt(II) were defined and the sorbent SiO_2-Met was applied for the determination of total Pt in cosmetic cream.

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REFERENCES

1. P. Kovacheva, R. Djingova, *Analytica Chimica Acta,* **464**, 7 (2002).
2. H. Mukai, Y. Ambe, M. Morita, *J. Anal. At. Spectrom*., **5**, 75 (1990).
3. K. Akatsuka, S. Hoshi, J. McLaren, S. Berman, *Bunseki Kagaku*, **43**, 67 (1994).
4. H. Mukai, Y. Ambe, M. Morita, *J. Anal. At. Spectrom.*, **5,** 75 (1990).
5. H. Bayrak, V. Bulut, M. Tufekci, H. Bayrak, C. Duran, M. Soylak, *Toxicological & Environmental Chemistry*, **99,** 590 (2017).
6. R. Sutherland, D. Pearson, C. Ottley, *Applied Geochemistry*, **22,** 1485 (2007)
7. A. Cantarero, M. Gomez, C. Camara, M. Palacios, *Anal. Chim. Acta*, **296**, 205 (1994).
8. B. Qu, *Analyst*, **121,** 139 (1996).
9. V. Otruba, M. Strnadová, B. Skalníková, *Talanta*, **40**, 22 (1993).
10. K. Jankowski, A. Jackowska, P. Łukasiak, *Analytica Chimica Acta*, **540**, 197 (2005).
11. K. Pyrzyńska, *Talanta,* **47**, 841 (1998).
12. B. Godlewska-Żyłkiewicz, *Microchim. Acta*, **147**, 189 (2004).
13. E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, *Microchemical Journal*, **101**, 59 (2012).
14. M. Osman, S. Kholeif, N. Abou-Almaaty, M. Mahmoud, *Anal Sci*, **20**, 847 (2004).
15. X. Wu, P. Liu, Q. Pu, Q. Sun, Z. Su, *Talanta*, **62**, 918 (2004).
16. Y. Yamini, M. Chaloosi, H. Ebrahimzadeh, *Talanta*, **56**, 797, (2002).
17. R. Vlašánkova, V. Otruba, J. Bendl, M. Fišera, V. Kanický, *Talanta*, **48,** 839 (1999).
18. P. Jal, S. Patel, B. Mishra, *Talanta*, **62,** 1005 (2004).
19. D. Bilba, D. Bejan, L. Tofan, *Croatica Chemica Acta*, **71**, 155 (1998).
20. P. Petrova, I. Karadjova, M. Chochkova, I. Dakova, M. Karadjov, *Bulgarian Chemical Communications*, Special Issue E, **95** (2017).
21. J. Sheehan, G. Hess, *J. Am. Chem. Soc*., **77**, 1067 (1955).
22. A. Bartyzel, E. Cukrowska, *Analytica Chimica Acta*, **707**, 204 (2011).
23. A. Bocca, G. Forte, F. Petrucci, A. Cristaudo, *Journal of Pharmaceutical and Biomedical Analysis*, **44**, 1197 (2007).
24. E. Guibal, N. Von Offenberg Sweeney, T. Vincent, J. Tobin, *Reactive and Functional Polymers*, **50**, 149 (2002).
25. V. Joshi, *Indian Natn. Sci. Acad*., **54,** 664 (1988).
26. D. Vermeulen, F. Cantwell, *Anal. Chem.*, **65,** 1360 (1993).