

SCHIFF BASES CHELATE SORBENTS FOR SEPARATION AND CONCENTRATION OF Pt FROM SEA WATER AND SPENT AUTOMOTIVE CATALYSTS

Petranka Petrova¹, Maya Chochkova¹, Olga Veleva², Metody Karadjov²

¹ South-West University "Neofit Rilski", Ivan Mihailov Str, 66
2700, Blagoevgrad, Bulgaria
E-mail: petya_dukova@yahoo.com

Received 11 January 2019

Accepted 30 July 2019

² Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev str. bl.24
1113 Sofia, Bulgaria

ABSTRACT

Schiff bases of 4-aminoantipyrine (Fig. 1, (a-d)) are synthesized and immobilized on silica gel to obtain 4 sorbents selective for Pt ions (Sig-Schiff^{a-d}). The extraction efficiency of the newly prepared sorbents toward Pt(II) and Pt(IV) is studied by a batch method and the application was performed in a column mode. The role of various parameters such as the sample acidity, the type and the concentration of the eluent, the sample and the eluent flow rates are optimized for a quantitative sorption of Pt(II) and Pt(IV). The influence of the different substituents in the benzylidene ring of the Schiff bases on the coordination properties of the sorbents and the extraction efficiency and selectivity toward Pt species is elucidated. It is found that the sorbents synthesized demonstrate a high selectivity toward Pt(II) - the quantitative sorption is achieved at high concentrations of HCl, whereas Pt(IV) has a poor sorption ability under identical experimental conditions. Moreover, the sorbents preserve their extraction capability and selectivity toward Pt(II) in acidic media even in presence of significant amounts of base metals. An analytical procedure is developed for Pt determination in surface waters and spent automotive catalysts.

Keywords: platinum group metals, solid phase extraction, ICP-OES, surface waters, spent automotive catalysts.

INTRODUCTION

Pt determination in various types of samples is of a practical importance but presents a challenging analytical task due to the low concentrations present and the spectral interferences observed. In most of the cases a separate determination of both oxidation states is desirable. Therefore an application of an enrichment step is indispensable for most of the analyzed samples – environmental (surface waters, road dust, soils, air samples), waste materials (spent automotive catalysts), geological samples. Solid phase extraction is conventionally used as an easy, simple and suitable method for a routine analytical practice procedure. The extraction efficiency of the sorbent determines the selectivity, the enrichment factor and the sensitivity of the developed analytical procedure. Various chelating and complex forming reagents supported on suitable materials have been recently synthesized.

The surface functional groups and the solid support are found to determine their extraction efficiency toward Pt species [1 - 4].

An important class of ligands for coordination of Pt refers to the aromatic nitrogen-containing heterocycle compounds, which offer the possibility of strong metal–ligand interaction. Schiff bases among them are promising coordinating agents for the development of sorption materials, first of all, due to the azomethine group in their structure and secondly, due to the vast possibilities to influence and regulate their chelating ability [5]. The 4-aminoantipyrine based heterocyclic Schiff bases combine some indispensable characteristics for noble metals complex formation, namely *N*-donor atoms for metal chelation, an aromatic ring providing an increased lipophilicity and substituents in the ring to enhance *N*-donor capacity [6 - 8]. In addition, the carbonyl group in their molecules is a potential donor due to the

large dipole moment (5.48 D), while the strong basic character makes them a very suitable ligand for solid phase extraction of metal ions [9]. However, no data have been reported for selective adsorption and extraction of precious metals by using this kind of ligands. Moreover, limited studies have discussed the applications of Schiff bases for quantitative determinations, mainly of some transition metals [10 - 11].

The focus of the present work is the elaboration of a sorption system based on 4-aminoantipyrine Schiff bases physically impregnated on silica gel for selective solid phase extraction of Pt species. The first stage refers to the synthesis of Pt selective ligands derived from Schiff bases of 4-aminoantipyrine and the development of Pt selective sorbents by impregnation of the ligands on silica gel. The second stage is devoted to the evaluation of the extraction efficiency of the newly developed materials and the establishment of the optimal conditions for selective enrichment of Pt species. An analytical procedure for the determination of Pt(II)/Pt(IV) in environmental samples is developed, characterized and applied to sea water and waste materials samples.

EXPERIMENTAL

Reagents

All chemicals were analytical reagent grade and were used without further purification. Stock solutions of Al(III), Cu(II), Fe(III), Mn (II), Ni (II) and Zn (II) ($1000 \mu\text{g mL}^{-1}$) in 2 % HNO_3 were provided by Titrisol, Merck (Darmstadt, Germany, www.merck.de). The stock standard solutions Pt(IV) ($1000 \mu\text{g mL}^{-1}$) in 5 % HC were purchased from Sigma-Aldrich (Germany). The working standard solutions were obtained by appropriate dilution of the stock standard solution. Silica gel for column chromatography ($\leq 0.063 \text{ mm}$ (≥ 230 mesh ASTM)), 4-aminoantipyrine and substituted benzaldehydes were purchased from Sigma-Aldrich Ltd. The pH adjustment was done by addition of HCl (Merck, 37 %).

Apparatus

All measurements were performed on ICP-OES spectrometer Ultima 2, Jobin Yvon under optimized instrumental parameters using Pt II 203.646 wave length for determination of Pt. The sample digestion was performed on microwave digestion system Model Milestone Ethos Touch Control (ETHOS TC). A centrifuge NEYA 8 Giorgio Bormac was used. A

peristaltic pump Ismatec ISM 829B was employed for column solid phase extraction. The pH measurements were conducted on a pH-meter (Hanna Instruments).

Synthesis of Schiff bases

The Schiff bases derived from 4-aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) and different substituted benzene carbaldehydes were sonochemically synthesized using the procedure described in our previous work [12].

The chemical structures of the products presented in Fig. 1(a-d) were confirmed by ^1H - and ^{13}C -NMR, IR and mass spectral data [13].

Sorbent Sig- Schiff^{a-d} preparation

The physical immobilization of the synthesized Schiff bases (Fig.1(a-d)) on silica gel was performed in two steps. The first step referred to an activation of the silica surface with concentrated HCl for 4 h under reflux and subsequent filtration, a washing and a drying in an oven at 150°C for 12 h. During the second step, the activated silica gel was refluxed separately with each of the Schiff bases in ratio 9:1 w/w in an acetone medium for 8 h. Finally, the sorbent was recovered from the acetone medium and dried at 40°C for 1 h [14].

Optimization experiments in a batch mode

Batch adsorption experiments were conducted by transferring 100 mg of Sig- Schiff^{a-d} in 15 ml centrifuge tube containing 10 ml of a standard solution of Pt(IV) with a concentration of $100 \mu\text{g L}^{-1}$ or a standard solution of Pt(II) with the same concentration ($100 \mu\text{g L}^{-1}$) in presence of 1 mL of 1 mol L^{-1} SnCl_2 to reduce quantitatively Pt(IV) to Pt(II). The total volume of the solution was 10 mL. A suitable amount of HCl was added in order to obtain acidity in the range of 0.001 mol L^{-1} HCl - 1 mol L^{-1} HCl. The suspension was agitated using a mechanical shaker for 20 min and then centrifuged. The collected effluat was measured by ICP-OES to determine the remaining metal. After sorbent Sig- Schiff^{a-d} washing with doubly distilled water, the retained Pt was eluted from the sorbent with a solution of thiocarbamide in HCl and quantified by ICP-OES. The kinetic of Pt sorption/desorption was investigated in a batch system after transferring 10 ml of Pt metal solution ($100 \mu\text{g L}^{-1}$) in the presence of SnCl_2 with 100 mg of Sig-Schiff^a at an optimal pH value and agitating the mixture in the time

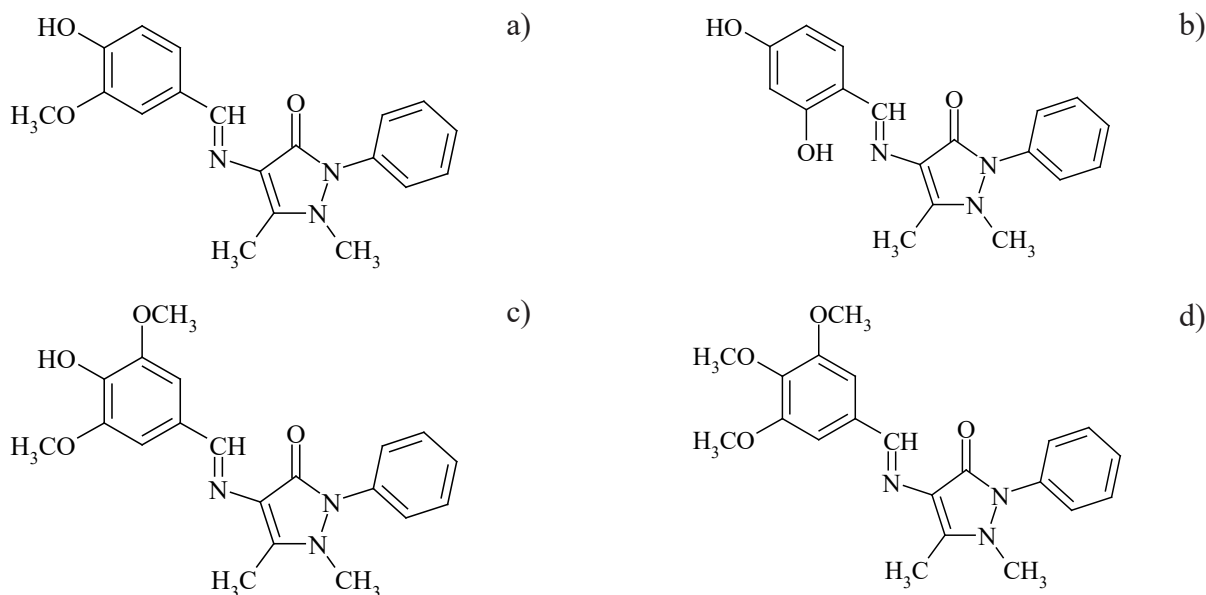


Fig. 1. A chemical structure of the Schiff bases synthesized.

interval for 5 min to 60 min. The amount of Pt in the effluates was determined by ICP-OES. The kinetics of desorption was studied after introduction of 500 μg Pt to 100 mg of Sig-Schiff^a and their subsequent elution within 5 min - 30 min.

Optimization of dynamic mode experiments in a column

The dynamic mode experiments were performed in a short glass column with an inner diameter of 10 mm and a length of 80 mm. It was equipped with porous frits on the top and the bottom. It was filled with 100 mg Sig-Schiff^{a-d}. The bottom of the column was connected to a peristaltic pump to regulate the flow speed. The column with the sorbent was initially washed with 1 mol L⁻¹ HCl. Then solutions of Pt(IV) or Pt(II) after reduction with tin (II) chloride were pumped through the column with a flow rate in the range of 2 mL min⁻¹ - 10 mL min⁻¹. Subsequently, the sorbent in the column was washed with doubly distilled water and a solution of thiourea in HCl was pumped through for Pt desorption. The eluent flow rate was varied in the range of 1 mL min⁻¹ - 5 mL min⁻¹. The effluates and eluates were analysed for Pt concentration by ICP-OES.

The degree of sorption (R_s %) was calculated using Pt amount in the initial sample solution (Q_{in}) and in the effuate (Q_{eff}) in accordance with the equation:

$$R_s \% = ((Q_{in} - Q_{eff}) / Q_{in}) \times 100,$$

The degree of elution (R_e %) was calculated using the amounts of Pt retained on the sorbent (Q_s) and Pt measured in the eluate (Q_{el}) using the following relation:

$$R_e \% = (Q_{el} / Q_s) \times 100.$$

Sample preparation

The sample of spent automotive catalysts (preliminary well homogenized by grinding) was weighed (0.25 g) and put into a Teflon digestion vessel. About 10 ml of aqua regia and 0.5 ml of hydrogen peroxide were added, the vessel was capped and placed in the carousel of the digestion system. The digestion was carried out in three steps: 300 W within 10 min followed by cooling down for 1 min; 600 W within 10 min followed by cooling down for 2 min and 1000W within 15 min. At the end of the program, the vessels were cooled to a room temperature in a fume hood and the pressure inside the vessels was slowly released. The cooled digested samples were transferred to 100 mL beakers, evaporated to near dryness, diluted with 0.5 mol L⁻¹ HCl and transferred with 0.5 mol L⁻¹ HCl to 100 ml volumetric flask. After filtration a sample of 45 mL was mixed with 1 mL of 1 mol L⁻¹ SnCl₂ in order to ensure reduction of Pt(IV) to Pt (II) and passed through the column filled with Sig- Schiff^a with flow rate 4 mL min⁻¹. The retained Pt(II) was eluted with 2 ml of 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl using an eluent flow rate of 2 mL min⁻¹.

RESULTS AND DISCUSSION

The synthesis of Schiff bases of 4-aminoantipyrine is relatively easy but their application as complexing ligands in a quantitative analysis is restricted because of their poor solubility in aqueous solutions and fast hydrolysis in acidic media [15 - 16]. On the other hand, SPE of platinum metals is favored in acidic media which makes the sample acidity a critical parameter for the sorption process. That is why the influence of HCl concentration on the degree of sorption of Pt(II) and Pt(IV) on Sig- Schiff^{a-d} is studied in a broad range from 0.001 mol L⁻¹ to 1 mol L⁻¹ HCl using a batch procedure. The results obtained indicate that the sorbents possess a high sorption efficiency (80 % - 97 %) towards Pt(II) in the whole acidic range studied (Fig. 2). Considering the sorption mechanism, it seems that although *N*-donor atoms contribute to metal chelation, the quantitative Pt sorption in highly acidic media could be attributed to an electrostatic attraction of negatively charged complexes [PtCl₄]²⁻ by protonated *N*-containing groups [17]. It is worth mentioning that an ion exchange mechanism has also been proposed by different researchers for the adsorption of chlorocomplexes of precious metals in HCl media on adsorbents modified by nitrogen containing ligands [3, 18].

On the other hand, the Schiff base stability and the rate of its hydrolysis depend strongly on the electronic nature of the substituent attached to the aldehyde moiety [19]. The data obtained in the literature reveal that the rates of hydrolysis in acidic media of Schiff bases

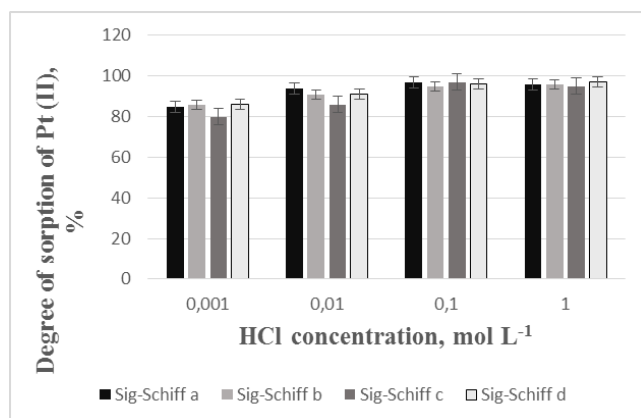


Fig. 2. HCl concentration effect on the degree of sorption of Pt(II) on Sig-Schiff^{a-d} in presence of SnCl₂ (10 ml standard solution of Pt(II) (100 µg L⁻¹) and 100 mg of Sig-Schiff^{a-d}, 20 min agitation time, three replicates).

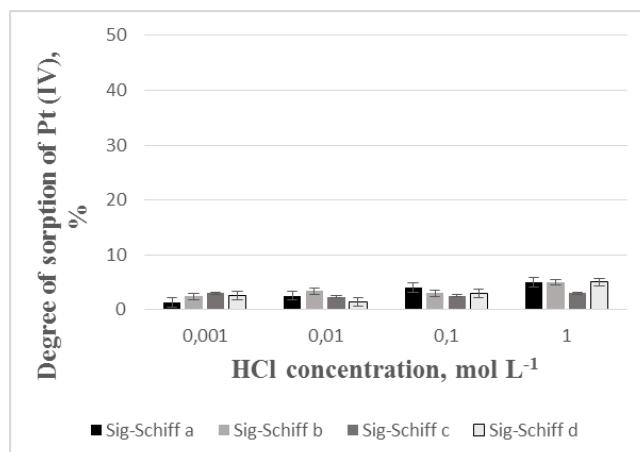


Fig. 3. HCl concentration effect on the degree of sorption of Pt(IV) on Sig-Schiff^{a-d} (10 ml of a standard solution of Pt(IV) (100 µg L⁻¹) and 100 mg of Sig-Schiff^{a-d}, 20 min agitation time, three replicates).

possessing an electron donating substituent decrease with acidity increase [20]. This is taken into account and HCl concentration in the range 0.1 M - 0.5 M HCl is selected as an optimum ensuring a high degree of Pt(II) sorption and a decreased rate of Schiff base hydrolysis.

Furthermore, the analogous experiments performed with Pt(IV) demonstrate that the sorption of kinetically inert chlorocomplexes of Pt(IV) is negligible in the whole acidity range studied (Fig. 3).

Usually, the heating of the sorbent containing solution or the use of a microwave radiation is recommended to facilitate the sorption of inert complexes [2]. An alternative approach could be referred to the introduction of a reducing agent prior to the sorption process leading to a more labile Pt(II). SnCl₂ in HCl [21], KI in H₂SO₄ [22] or ascorbic acid [23] are used for that purpose. A solution of SnCl₂ is used in the present work for the reduction of Pt(IV) prior to sorption on Sig-Schiff^{a-d}. The difference in the sorption behavior of Pt(II) and Pt(IV) in respect to Sig-Schiff^{a-d} can be successfully used for Pt speciation analysis, quantifying initially only Pt(II) and then the total Pt content by using SnCl₂. This provides the estimation of Pt(IV) presence on the ground of the difference between the two experimental values obtained.

The process of desorption of Pt retained on Sig-Schiff^{a-d} is studied in a batch mode. The desorbing agent is selected taking into account the sorption mechanism which is dominated by the chelation and the electrostatic attraction. This suggests the choice of an eluent with *N*- and *S*- donor atoms, which will be subsequently pro-

tonated in acidic media forming a stable complex with Pt. A solution of thiourea in HCl is most frequently used as an eluent. The experiments performed with varying concentrations of thiourea and HCl reveal that 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl is the most favorable eluent ensuring a quantitative desorption of retained Pt. The optimal eluent volume is studied in the range from 2 mL to 10 mL. It is found that 2 mL of the eluent solution are enough to desorb quantitatively Pt from the sorbent. The influence of the sample volume passed through the column is examined in the range from 5 mL to 200 mL and it is found that Pt extraction efficiency is above 95 % up to 50 mL sample volume.

The results from the sorption/desorption studies show that there is no difference in the extraction ability of the different Schiff bases sorbents (Sig-Schiff^{a-d}). It is assumed that the type of the substituents and their positions in the aromatic ring are not essential for the mechanism of the sorption process. In view of the fact that all sorbents prepared behave in an identical manner through their common azomethine group, carbonyl oxygen and *N*-heterocycle, the further experiments are carried out with Sig-Schiff^a.

The sorption kinetics is studied under optimized conditions in a batch system. The effect of the contact time on Pt(II) adsorption using Sig-Schiff^a is presented in Fig. 4. It is seen that the adsorption process is fast, reaching a value close to 100 % within 40 min - 45 min. The time dependence of Pt desorption determined in case of an optimal eluent composition shows that 20 min ensure the quantitative recovery of Pt retained.

The dynamic column mode is a preferable approach to perform solid phase extraction in case of a routine

laboratory practice. The experiments are conducted in a dynamic mode using a glass column filled with 100 mg of Sig-Schiff^a sorbent. A sample solution of Pt (100 µg L⁻¹) in 1 mol L⁻¹ HCl and 1 mL of 1 mol L⁻¹ SnCl₂ with a final volume of 10 mL is passed through the column with different flow rates, namely 2 mL min⁻¹, 4 mL min⁻¹, 6 mL min⁻¹, 8 mL min⁻¹ and 10 mL min⁻¹. It is found that the sample flow rate of 4 mL min⁻¹ ensures a quantitative sorption of Pt(II). The retained Pt (II) on Sig-Schiff^a is eluted with 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl. The complete elution of the analyte is achieved using an eluent flow rate of 2 mL min⁻¹.

The selectivity of the sorbent toward base metals is studied in a column mode under optimized conditions. The effect of the various matrix ions on the degree of sorption of Pt (II) is examined: 10 mL solution containing Pt (II) (100 µg L⁻¹) and base metals (Al, Cu, Fe, Mn, Ni, and Zn) is passed through the column packed with 100 mg Sig-Schiff^a under optimized conditions and a sample flow rate of 4 mL min⁻¹. It is found that the interfering metals do not affect the retention of Pt on the sorbent. An extraction efficiency of 96 % is reached (Table 1). Furthermore, the experiments reveal that the extraction of the base metal ions, i.e. Al(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II), is negligible under the experimental conditions used demonstrating the high selectivity of Sig-Schiff^a sorbent toward Pt(II) in HCl solutions and its potential application for Pt determination in a complicated matrix. The extraction of the retained Pt complexes from the sorbent is conducted using 2 mL of 0.7 mol L⁻¹ thiourea in 2 mol L⁻¹ HCl with an optimal flow rate of 2 mL min⁻¹. The recovery reached is within the range of 95 % - 96 %.

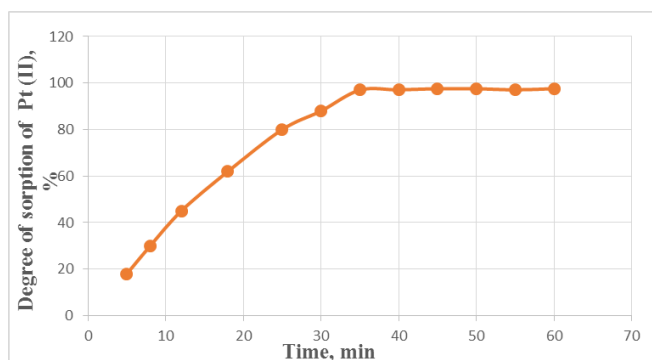


Fig. 4. A contact time effect on the degree of sorption of Pt(II)/SnCl₂ on Sig-Schiff^a (10 mL standard solution of Pt(II) (100 µg L⁻¹) and 100 mg of Sig-Schiff^{a-d}).

Table 1. Matrix ions effect on Pt(II) extraction using Sig-Schiff^a.

Ions	Concentration (mg L ⁻¹)	Extraction (%)
Al (III)	100	20±3
Zn (II)	100	15±4
Ni (II)	100	<1
Mn (II)	100	<1
Cu (II)	200	<1
Fe (III)	100	<1
Pt (II)	0.1	96±5

Table 2. Added/found method for Pt(II) in seawater. Three parallel determinations.

Sample	Pt(II)		
	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$ [mean \pm s]	R _E , %
Sea water	0	BDL*	-
Sea water	5.00	5.23 \pm 0.21	104.6
Sea water	10.00	9.89 \pm 0.24	98.9
Sea water	20.00	19.78 \pm 0.42	98.9

* Below detection limits

Determination of Pt in waste materials (spent automotive catalysts)

The content of Pt in spent automotive catalysts varies in a wide range from very low amounts to directly measurable concentrations. An application of preliminary enrichment is inevitable in some cases especially in presence of high concentrations of base metals. The accuracy and the precision of the analytical procedure advanced are verified through the application of an added/found method and an analysis of samples of a known Pt content. The recovery of Pt (II) obtained by the added/found method varies between 90 % - 95 % with a relative standard deviation in the range from 5 % to 9 %. The comparison between the results obtained by the proposed analytical procedure and the known values for Pt content in samples of spent automotive catalysts shows a very good agreement. The determination limit achieved is $0.9 \mu\text{g g}^{-1}$. It is based on ten times standard deviation of the blank sample (10σ criteria).

Determination of noble metals in sea water

The analytical application of prepared Sig-Schiff was tested through Pt recovery studies. The noble metal ions are spiked to 100 mL sea water samples at three different levels ($5 \mu\text{g L}^{-1}$, $10 \mu\text{g L}^{-1}$ and $20 \mu\text{g L}^{-1}$) under optimal experimental conditions and then passed through a column filled with 100 mg of a sorbent with a flow rate of 4 mL min^{-1} . The retained ions are eluted with 2 mL thiourea in HCl and quantified by ICP-OES. As evident from Table 2, the added and measured amounts amount of the analyte are in agreement (Student's t-test, $\alpha = 95 \%$) verifying the accuracy of the procedure. The precision of the method, expressed by the relative standard deviation (RSD) under optimum conditions, is determined by performing 3

replicates obtaining RSD from 2 % - 4 % in the concentration range from $5 \mu\text{g L}^{-1}$ to $20 \mu\text{g L}^{-1}$ Pt(II). The detection limits (LOD) defined as three times the standard deviation of the blank sample are found to be $0.002 \mu\text{g L}^{-1}$.

CONCLUSIONS

New sorbents based on silica gel modified by Schiff bases (Sig-Schiff^{a-d}) are applied aiming an effective and selective separation and enrichment of trace amounts of Pt in presence of base metals. It is found that Pt(II) are quantitatively extracted in acidic medium whereas Pt(IV) are not retained. It is established that the Schiff bases of 4-aminoantipyrine containing different substituents behave in a similar way and are suitable ligands for sorption and recovery of chloride complexes of Pt(II). The applicability of the sorbents to Pt determination in environmental samples and waste materials is examined by the added/found method and recovery experiments with laboratory certified samples. The results obtained demonstrate a high extraction efficiency and selectivity of Sig-Schiff^a as a sorbent for column solid phase extraction of Pt.

Acknowledgements

The authors gratefully acknowledge the financial support (grant RP-A11/18) provided by South-West University "Neofit Rilski", Blagoevgrad, Bulgaria.

REFERENCES

1. R. Vlašánková, L. Sommer, Solid Phase Extraction and Preconcentration for the Determination of Trace Amounts of Platinum Group Metals in Environmental and Biotic Material. A Critical Review, Chem. Papers, 53, 1999, 200-209.
2. O. Mokhodoeva, G. Myasoedova, I. Kubrakova,

- Preconcentration of noble metals with the POLYORGS 4 complexing sorbent under the action of microwave irradiation, *J Anal Chem*, 62, 2007, 406-410.
3. M. Gurung, B. Adhikari, S. Morisada, H. Kawakita, K. Ohto, K. Inoue, S. Alam, N-aminoguanidine modified persimmon tannin: A new sustainable material for selective adsorption, preconcentration and recovery of precious metals from acidic chloride solution, *Bioresource Technology*, 129, 2013, 108-117.
4. S. Bratskaya, A. Ustinov, Y. Azarova, A. Pestov, Thiocarbamoyl chitosan: Synthesis, characterization and sorption of Au(III), Pt(IV), and Pd(II), *Carbohydrate Polymers*, 85, 2011, 854-861.
5. G. More, D. Raut, K. Aruna, S. Bootwala, Synthesis, spectroscopic characterization and antimicrobial activity evaluation of new tridentate Schiff bases and their Co(II) complexes, *Journal of Saudi Chemical Society*, 21, 2017, 954-964.
6. J. Hagemann, P. Kaye, Designer ligands. Part 3: Synthesis of PGMspecific bidentate and tridentate ligands, *Tetrahedron* 55, 1998, 869-874.
7. J. Hagemann, P. Kaye, (). Designer ligands. Part 4: Synthesis of acyclic and macrocyclic tetradentate platinum group metal-specific ligands, *J. Chem. Soc. Perkin Trans.*, 1, 1999, 341-347.
8. P. Kaye, Designer ligands: The search for metal ion selectivity, *S. Afr. J. Sci.*, 107, 2011, 1-8.
9. P. Deshmukh, P. Soni, A. Kankoriya, A. Halve, R. Dixit, 4-Aminoantipyrine: A Significant Tool for the Synthesis of Biologically Active Schiff Bases and Metal Complexes, *Int. J. Pharm. Sci. Rev. Res.*, 34, 2015, 162-170.
10. N. Bader, Applications of Schiff's bases chelates in quantitative analysis: A review, *Rasayan J. Chem.*, 3, 2010, 660-670.
11. M. Koluman, F. Tokay, S. Bagdat, Schiff base immobilized silica gel framework as an efficient sorbent for preconcentration of Pb and Zn ions in aqueous media, *Turk. J. Chem.*, 40, 2016, 953-964.
12. P. Petrova, I. Karadjova, M. Chochkova, I. Dakova, Solid phase extraction of Au(III) using silica gel modified with 4- aminoantipyrine Schiff bases, *Chemistry: Bulgarian Journal of Science Education*, 24, 2015, 441-448.
13. M. Chochkova, B. Stoykova, I. Romanova, P. Petrova, I. Tsvetkova, H. Najdenski, L. Glomb, N. Nikolova, G. Ivanova, A. Chapkanov, T. Milkova, M. Štícha, I. Nemec, Sonochemical synthesis of 4-aminoantipyrine schiff bases and evaluation of their antimicrobial, anti-tyrosinase and DPPH scavenging activities, *Chemistry: Bulgarian Journal of Science Education*, 27, 2018, 897-914.
14. P. Petrova, I. Karadjova, M. Chochkova, I. Dakova, M. Karadjov, New amino acid modified silica gel sorbents for solid phase extraction of Au (III), *Bulgarian Chemical Communications, Special Issue E*, 2017, 95-100.
15. G. In, Y. S. Kim, J. Choi, Study on Solvent Extraction Using Salen(NEt₂)₂ as a Chelating Agent for Determination of Trace Cu(II), Mn(II), and Zn(II) in Water Samples, *Bull. Korean Chem. Soc.*, 29, 5, 2008, 969-973.
16. N. Bader, Schiff's bases complexation and solid phase extraction for improved trace element analysis, Thesis, 2009.
17. P. Chassary, T. Vincent, J. Marciano, L. Macaskie, E. Guibal, Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, *Hydrometallurgy*, 76, 2005, 131-147.
18. T. Buslaeva, H. Ehrlich, S. Samsonova, N. Bodnar, I. Rudik, P. Mingalev, G. Lisichkin, Interaction of platinum metals ions with ligands attached to silica surface, *Proceedings of the 27th International Chugaev Conference on Coordination Chemistry*, Novgorod, Russia, 2017, 23.
19. H. Hassib, N. Abdel-Kader, Y. Issa, Kinetic Study of the Hydrolysis of Schiff Bases Derived from 2-Aminothiophenol, *J. Solution Chem.*, 41, 2012, 2036-2046.
20. E. Cordes, K. Jencks, The Mechanism of Hydrolysis of Schiff Bases Derived from Aliphatic Amines', *Hydrolysis of Schiff Bases*, 85, 1963, 2843-2848.
21. K. Koch, D. Auer, Determination of platinum and palladium in strongly acid solution by means of flow injection analysis, *Talanta*, 40, 12, 1993, 1975-1980.
22. Z. Marzenko, S. Kus, Separation and spectrophotometric determination of palladium and platinum with dithizone using an iodide medium, *Analyst*, 110, 1985, 1005-1009.
23. E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, Column solid phase extraction and determination of ultra-trace Au, Pd and Pt in environmental and geological samples, *Microchemical Journal*, 101, 2012, 59-64.