RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Preconcentration of Ag and Pd ions by using graphite oxide and 2,6 diaminopyridyne from water, anode slime and catalytic converter samples

Gülşen Yıldırım, Şerife Tokalıoğlu*, Halil Şahan, Şaban Patat

In this work, the graphite oxide was used for the first time as an effective adsorbent for the separation/preconcentration of the Ag and Pd ions in from various samples prior to flame atomic absorption detection. 2,6 diaminopyridyne was used as a chelating reagent. Analytical parameters affecting the solid phase extraction of Ag and Pd such as pH, adsorption and elution contact time, centrifuge time, reagent amount, eluent concentration and volume, sample volume and matrix ions were investigated. The recovery values for Ag and Pd were found to be ≥95%. The adsorption and elution contact times were 60 s. The preconcentration factor of the method was 120 for a 600 mL sample by using 100 mg of the graphite oxide. The elution was easily made with 5 mL of 2.0 mol L^{-1} HCl. The reusability of the graphite oxide was 150. The detection limits of Ag and Pd were 0.39 μg L^{-1} and 0.94 μg L^{-1}, respectively. The relative standard deviations (RSD, %) were ≤2.5%. The proposed method was validated by analysing the certified reference materials, SRM 2556 (Used Auto Catalyst Pellets) and TMDA-70 Lake water, and spiked real samples. The optimized method was applied for the preconcentration of Ag and Pd ions in various water (tap water, mineral water and wastewater), anode slime and catalytic converter samples.

Erciyes University, Faculty of Science, Chemistry Department, TR-38039, Kayseri, Turkey.
E-mail: serifet@erciyes.edu.tr

1   Introduction

Heavy metals are highly toxic at low concentrations and can accumulate in living organisms, causing several disorders and diseases. Among them, silver and palladium are both valuable metals and pollutants. Silver ion is one of the most toxic forms of a heavy metal, surpassed only by mercury and thus has been assigned to the highest toxicity class, together with cadmium, chromium (VI), copper, and mercury.[1] Silver can be assimilated from the lungs, gastrointestinal tract, mucous membranes, and skin.[2] But, it is a lustrous noble metal with the highest electrical and thermal conductivity of all elements. As a consequence of these characteristics, it has a wide variety of applications in electronics, batteries, conductive pastes, silverware, jewelry etc. It is also used in photography, brazing alloys and solders, to disinfect drinking water and as an antibacterial agent. Many medical devices and implants are treated with silver to reduce the risk of infection. The growing application of silver in medicine and industry, its entrance in the environment has been increased.[3-5]

Palladium is a metal of economic importance due to its extensive use in metallurgy, in various chemical syntheses, the production of dental and medicinal devices and in jewellery. One of the most important applications of Pd is the production of catalytic converters for car engines. [6,7] The increasing uses of platinum group elements in vehicle exhaust catalysts, in addition to some other applications cause their anthropogenic emission and spread in the environment.[8]

The separation and recovery of Ag and Pd ions from base metal ions as well as the development of selective and accurate methods for determination of precious metals in waste and different environmental compartments are an important research area.[6, 9-12] Solid phase extraction (SPE) is the most widely used method for these purposes. It is a very effective and versatile tool for the separation and preconcentration of Ag and Pd. Several important features

of the sorbents used defines its applicability and efficiency-high preconcentration factors, fast complex formation, high stability constant of the complex formed and low backpressure of the column.[9, 10, 13]

Several studies on sorbents and their use for preconcentration and separation of Ag and Pd ions have been reported. Some examples are: Sepabeads SP207,[14] chelating resin,[15,16] cysteine modified silica gel,[13] agarose coated magnetic nanoparticles,[7] silica gel,[17] chloromethylated polystyrene polymer modified with 2-mercaptobenzothiazole,[18] magnetic nanoparticles (MNPs) coated by 3-(trimethoxysilyl)-1-propantiol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole,[19] imprinted polymer,[6] and dithiocarbamate coated fullerene C60.[20]

New discoveries in materials science may provide new tools for analytical sample preparation. An example is the wide use of carbon nanomaterials in solid-phase extraction (SPE).[21] Graphite oxide (GO) is a layered structure carbonaceous material and obtained through the reaction of graphite with strong oxidants such as potassium permanganate in concentrated sulfuric acid. It is known that it consists of randomly distributed regions of unoxidised (aromatic) graphite and regions of aliphatic six-membered rings, rich in oxygen-containing functional groups, including epoxys, hydroxyls and carboxylic groups.[22,23] Recently, few investigations have been reported on GO applications for adsorption such as humic acid,[22] tetracycline antibiotics,[24] aromatic organic contaminants,[25] methylene blue[26] and U(VI).[27] **The reported results show that GO exhibits strong and high adsorption capacity.**

In this study, GO as an adsorbent and 2,6 diaminopyridyne (dap) as a complexing reagent for the removal of Ag and Pd from aqueous solutions were used. **2,6-diaminopyridine is a familiar and simple organic dye which contains two amino and one pyridine ring.**

Experimental conditions such as the pH, adsorption and elution contact time, reagent concentration, eluent type and concentration, sample volume were investigated in detail. To our knowledge, there has been no report yet about the use of GO and dap for the separation and preconcentration of Ag and Pd ions from various samples.

2 Experimental

2.1 Instrument

Silver and palladium determination were made by an A Perkin Elmer AAnalyst 800 model (Waltham, MA, USA) flame atomic absorption spectrometry in an air-acetylene flame (2.0-17 L min^{-1}). Ag and Pd hollow cathode lamps as the radiation source were used for absorbance measurements with wavelengths of 328.1 nm and 244.8 nm, respectively. A WTW pH315i digital pH meter equipped with a combined pH electrode was used for checking the pH of solutions. A Clifton NES 280 model shaker and Wiggen Hauser VM model vortex were used in the works. The characterization GO was performed by using LEO 440 model scanning electron microscopy (SEM) with an accelerating voltage of 20 kV and BRUKER AXS D8 Advance model X-ray diffractometer using Cu Kα radiation (λ= 0.15406 nm) in the range of 2θ =10–90°. The Fourier Transform Infrared (FT-IR) spectrum was recorded on a Perkin-Elmer Spektrum 400 FT-IR spectrometer in the form of KBr pellets.

2.2 Reagents and solutions

All chemicals were of analytical grade and were used without further purification. All solutions were prepared using ultra-high purity water from a Milli-Q system (18.2 MΩ cm, Millipore). Ag and Pd stock solutions (1000 μg mL^{-1}) were purchased from Sigma-Aldrich. Working standard solutions of Ag and Pd were prepared daily by dilution of their stock solutions. The 1.0%(w/v) solution of 2,6 diaminopyridyne (dap) was prepared daily by dissolving 1.0 g of reagent (Sigma-Aldrich) in 100 mL of ethyl alcohol. The following

solutions were used for various pHs: diluted acid for pH 1, H_3PO_4/NaH_2PO_4 for pH 2 and 3, CH_3COOH/CH_3COONa for pH 3.5-6, CH_3COONH_4 for pH 7, and NH_3/NH_4Cl for pH 8 and 9.

2.3 Synthesis of graphite oxide

The GO was synthesized from natural graphite (Merck) by a Hummers method as described elsewhere.[28,29] Before use, in order to remove adsorbed impurities, graphite oxide was washed with 2 mol L^{-1} HCl and then ultra high purity water (see Supplementary material).

2.4 Solid phase extraction procedure

The pH of 20 mL of model solution including 20 µg Pd, 10 µg Ag and 100 mg of the GO was adjusted to 4. **1 mL reagent (dap) of 1% (w/v) was added to the solution.** The solution was mixed for 1 min by vortexing to facilitate adsorption of Ag and Pd on the GO and then was centrifuged at 4000 rpm for 5 min. The supernatant was removed by micropipette. 5 mL of 2 mol L^{-1} HCl was used as eluent. After vortexing for 1 min and centifuging for 5 min, Ag and Pd concentrations in eluate were determined by FAAS.

For the optimization of sample volume, a glass column (100 mm in length and 10 mm in diameter) was used. A 100 mg of the GO was slurried in water and then poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the adsorbent. The column was preconditioned by pH 4 buffer solution. The model solution prepared at pH 4 was passed through the column at a flow rate of 2 mL min^{-1}. The adsorbed Ag and Pd ions were eluted with 5 mL of 2 mol L^{-1} HCl. Ag and Pd concentrations in eluate were determined by FAAS.

2.6 Sample pretreatment and dissolving procedures

Tap water, mineral water, and wastewater samples were obtained from the our research laboratory, local market, and Organized Industrial Region of Kayseri, Turkey, respectively. The wastewater sample was filtered through 0.45 μm pore size membrane filter to remove suspended particulate matter. 250 ml of tap water, 100 mL of mineral water and 50 mL of wastewater samples were used for the analyses of Ag and Pd.

Portions of 0.020 g of catalytic converter sample, 1.00 g of anode slime and 0.025 g of standard reference material 2556 (Used Auto Catalyst Pellets) were used for analysis. The SRM 2556 was calcined for 2 h at 500 °C prior to analysis to assure a stable weighing form.

The digestion of anode slime was made by 10 mL aqua regia twice. The evaporation procedure was carried out on a hot plate at about 100 °C. The insoluble parts were filtered through a blue band filter paper by ultra high purity water.[14,15] The filtrate was diluted to a volume of 20 mL by ultra-high purity water and the preconcentration procedure described above was applied to the sample solutions.

The catalytic converter sample and standard reference material 2556 were put into a 100 mL teflon beaker separately. 10 mL of aqua regia was added to the beaker. The mixture was evaporated near to dryness on a hot plate at about 100 °C. 10 mL of aqua regia was added again to the residue and the mixture was again evaporated near to the dryness. Then 3 mL HF was added to the residue.[30] After evaporation, the interior surface of the beaker was washed by ultra-high purity water and filtered through a blue band filter paper. The pH of the filtrate was adjusted to 4 and the solution was diluted to 20 mL with ultra-high purity water. The preconcentration procedure described above was used to separate and preconcentrate of Ag and Pd.

3 Results and Discussion

3.1 Characterization of GO

The XRD patterns of pristine natural graphite and GO are shown in Fig. 1. As shown in Fig 1b, the dissappearance of native graphite peak, between 2θ of $25°$ and $30°$, reveals the complete oxidation of graphite. In addition, Fig 1 shows that, the most intensive peak $2\theta=12°$ corresponds to the (001) reflections of GO, and the inter layer spacing (0.77 nm) is much larger than that of natural graphite (0.36 nm) due to introduction of oxygen containing functional groups on the graphite sheets.

The morphology and microstructure of the graphite and GO are shown in Fig. S1. Single flakes of GO may be observed. GO flakes have relatively large surface (with the edge of sheets about the size of micrometers) and its morphology resembles thin curtain.

Fig. 2 shows the FTIR spectra of graphite and GO. The characteristic vibrations for GO include the broad and intense O-H peak 3186 cm^{-1}, strong C=O peak in carboxylic acid and carbonyl moieties at 1715 cm^{-1}, C-OH peak at 1372 cm^{-1}, C-O-C peak at 1224 cm^{-1}, C-O streching peak at 1038 cm^{-1}, and aromatic C-H peak at 589 cm^{-1}.The peak centered at 1590-1620 cm^{-1} can be assigned to the vibrations of the adsorbed water molecules, but may also contain components from the skeletal vibrations of unoxidized graphitic domains. [31,32]

3.2 Effect of pH

The acidity of the sample solution is usually the most critical parameter on the SPE studies of metal ions because pH value affects the adsorption efficiency.[33,34] The effect of the sample pH on the adsorption of Ag and Pd on the GO was studied at different pH values from 1 to 9 in model solutions containing 1 mL reagent of 1% (w/v), 20 µg Pd and 10 µg Ag. As can be seen in Fig. 3, Ag and Pd were adsorbed 90-95 % in the range of pH 3.0-4.5. At pH 4, the

recovery values for both metal ions were quantitative (95%). At lower pHs (≤3), the recovery values of Ag and Pd decrease, due to the competition between protons and the analytes for occupying the active sites. At higher pH values, the hydrolysis of cations may occur. Therefore, pH 4 was selected for all the subsequent studies. **The described method for the Au, Co, Cu, Fe, Mn, Ni, Cr, Pb, Cd and Zn at pH 4 was also applied. The recovery values changed in the range of 14-88%.**

3.3   Effect of contact time on the adsorption and elution and also centrifuge time

The effect of contact time on the adsorption and elution of the Ag and Pd ions was examined for different vortexing times (10, 30, 45, 60, 90 and 120 s). The results are shown in Fig. 4. The vortexing time of 60 s was enough for both adsorption and elution of Ag and Pd ions. So, 60 s was used to be both adsorption and elution contact times for the subsequent experiments. The short time to reach equilibrium show that the GO-metal interactions is rather rapid.

Also, the effect of centrifuge time after adsorption of Ag and Pd ions was studied for 2, 3, 4, and 5 min at 4000 rpm. The quantitative recovery values for both Ag and Pd were obtained for 5 min. So 5 min was selected as centrifuge time.

3.4   Effect of reagent (dap) amount

The effect of 2,6 diaminopyridine amount on adsorption of Ag and Pd was studied by using different volumes from 0 to 2 mL (20 mg) of 1% (w/v) reagent. The effect of reagent amount is shown in Fig. 5. The recoveries of Ag and Pd were quantitative (95%) for reagent amounts of 1.0 mL (10 mg). Without adding reagent, the recovery values for both Ag and Pd were found to be 73%. Therefore 1.0 mL reagent amount was chosen for the subsequent experiments.

3.5   Effect of type, volume and concentration of eluting reagent

The important factor that affect the preconcentration technique is the type, concentration and volume of the eluent used for the release of the Ag and Pd ions from adsorbent.[35] Thus, various concentrations of HNO_3 and HCl of 5 mL were tested. Optimization was performed to achieve the quantitative recovery with the minimal concentration and volumes of the eluent. The results (Table 1) revealed that 2 mol L^{-1} HCl solution was sufficient for quantitative elution of the adsorbed Ag and Pd. **The HCl forms anionic chloro complexes with Ag and Pd ions and strippes them from sorbent.** The effect of 2 mol L^{-1} HCl volume (1-6 mL) on the recovery of Ag and Pd was also studied. The quantitative recovery values could be obtained with 5 mL of 2 mol L^{-1} HCl. So, the eluent volume was optimized to be 5 mL.

3.6   Effect of sample volume

In solid phase extraction studies, the sample volume is one of the important parameters to obtain high preconcentration factor. The effect of sample volume on the recovery of Ag and Pd was investigated by model solutions of 100-750 mL and the column method given in section 2.4 was used. The recovery values of Ag and Pd were found to be in the range of 91-96% for the sample volume of 600 mL (Fig. 6). Thus, the preconcentration factor for Ag and Pd was 120 based on 5 mL eluent volume.

3.7   Reusability of the GO

In order to examine the stability and potential regeneration of the GO, adsorbent was subjected to several adsorption-elution cycles. The recovery values for Ag and Pd were monitored. The adsorbent of 100 mg was reused after regenerated with 5 mL of 2 mol L^{-1} HCl and then 5 mL of ultra pure water, respectively. The cycle results show that the adsorbent is stable up to 150 runs without decrease in the recoveries of Ag and Pd and it can be reused.

3.8   Effects of coexisting ions

Investigating the matrix ion effects of the real samples is an important point for preconcentration/separation studies.[36] Interfering effect of matrix ions such as Na(I), K(I), Ca(II), Mg(II), Fe(III), Zn(II), Cu(II), Al(III), Ni(II), Cd(II), Mn(II), Cr(III), Pb(II), Au(III), Co(II), SO_4^{2-}, Cl^-, and PO_4^{3-} on adsorption of 10 µg Ag and 20 µg Pd in model solutions was studied under optimum experimental conditions. The tolerance limit is considered as the concentration of interfering ions that reduce extraction efficiency of Ag and Pd ions to 90%. The recovery value are shown in Table 2. It can be seen that the developed method is useful for determining Ag and Pd in the various water, anode slime and convertor samples.

Also the some matrix components of the anode slime sample determined by FAAS without using the described separation/ preconcentration method and the metal concentrations found in the eluate solution after applying the described method are shown in Table 3. **Ag concentration in the anode slime was not detected by FAAS measurement without using the separation/preconcentration step, but it was found to be 22 µg g^{-1} by applying the described method. The method separates successfully the Ag ions from the anode slime matrix.** These results show that a separation/preconcentration method is required for the determination of Ag in anode slime. In our previous study, it was described that a separation method for the determination of Pd in catalytic converter samples is necessary.[17]

3.9   Adsorption isotherm and adsorption capacity

The adsorption isotherms and adsorption capacity of GO for Ag and Pd were studied under optimal experimental conditions. For model solutions of 20 mL containing 100 mg GO and 5-500 µg mL^{-1}of Ag and Pd adjusted to pH 4, the described method was applied. The eluent was diluted 10 or 20 fold. As shown in Fig. 7a for Ag and Fig. 7b for Pd, the adsorption data were

fitted according to the linear form of the Langmuir isotherm model based on the following equation: [36]

$$\frac{C_e}{q_e} = (\frac{1}{K_L q_m}) + (\frac{C_e}{q_m})$$

where q_e and C_e are the Ag and Pd amounts adsorbed (mg g^{-1}) and the Ag and Pd concentrations in solution (µg mL^{-1}), respectively, at equilibrium. K_L is the Langmuir constant (L mg^{-1}) and q_m is the maximum adsorption capacity of the adsorbent (mg g^{-1}). Langmuir isotherm was used to determine the q_m and K_L values from the linear coefficients obtained by plotting C$_e$/q_e as a function of C_e. The adsorption capacities were found to be 1.82 mg g^{-1} for Ag and 6.39 mg g^{-1} for Pd.

3.10 Analytical figures of merits

The detection limit (DL, 3s/b, n=13) of the solid phase extraction method for Ag and Pd was calculated under optimum experimental conditions after application of the preconcentration method to blank solutions. In the calculation of DLs, preconcentration factor of 120 was used. [37] The DL calculated as three times the standard deviation of the blank solutions divided by the slope of the calibration curve of the method was found to be 0.39 µg L^{-1} for Ag and 0.94 µg L^{-1} for Pd. The limit of quantifications (10s/b) for Ag and Pd were 1.32 µg L^{-1} and 3.15 µg L^{-1}, respectively. The relative standard deviations (RSD, %, n=10) were found to be 1.6% for Ag and 2.5% for Pd, which indicated that the described method has a good precision.

3.11 Validation and applications of the method

In order to validate the accuracy of the method, certified reference materials (SRM 2556 Used Auto Catalyst and TMDA-70, lake water) were analysed. The results are listed in Table 4. The obtained results were in good agreement with the certified values. The described method

was applied to the determination of Ag and Pd in tap water, mineral water, wastewater, anode slime and converter samples. In addition, the recovery experiments of spiked amounts of Ag and Pd were carried out. The results obtained are given in Tables 5 and 6. The recovery values of Ag and Pd were found to be in the range of 95-109%.

3.12 Comparison with other solid phase extraction methods

The comparative data from some recent papers on solid phase extraction of traces Ag and Pd on the various adsorbents are given in Table 7. The time to attain equilibrium for several adsorbent was reported to be long. In this work, the short contact time (60 s) for both adsorption and elution showed that the GO-metal interaction is rather rapid. The reusability of the adsorbent was rather well. The detection limit, preconcentration factor of the method and precision are comparable and/or better than those of the other methods. The adsorption capacity of GO for Ag was generally higher than the other adsorbents.

4 Conclusion

In this study, a new, simple, selective, accurate, rapid, low cost, and environmentally friendly solid phase extraction method by using GO as an adsorbent was developed for the first time for preconcentration of Ag and Pd ions in various water, anode slime and convertor samples. The adsorbent exhibited a good stability. It could be used for 150 cycles. The method showed high tolerance limit to remove matrix ions in real samples. The preconcentration factor of the method was 120. The adsorption and elution of Ag and Pd ions were succesfully made within 1 min. The acidic working pH (4), good precision ($\leq$2.5%) and low detection limits (0.39 and 0.94 μg L^{-1}) are the other important properties of the described method. The method can be used for Ag and Pd preconcentration from various water, anode slime and converter samples in routine analysis laboratories.

References

1. H. T. Ratte, *Environ. Toxicol. Chem.,* 1999, **18**, 89–108.

2. A. R. Firooz, A.A. Ensafi, N. Kazemifard, R. Khalifeh, *Sens. Actuators B,* 2013, **176,** 598– 604.

3. R. G.O. Araujo, F. Vignola, I. N.B. Castilho, B. Welz, M. G. R. Vale, P. Smichowski, S. L.C. Ferreira, H. B.-Ross, *Microchem. J.,* 2013, **109,** 36–40.

4. I. D. Schrijver, M. Aramendia, L. Vincze, M. Resano, A. Dumoulin, F. Vanhaecke, *Spectrochim. Acta Part B,* 2007, **62,** 1185–1194.

5. W. Guo, S. Hu, J. Zhang, H. Zhang, *Sci.Total Environ.,* 2011, **409**, 2981–2986.

6. B. G.-Zyłkiewicz, B. Leśniewska, I. Wawreniuk, *Talanta,* 2010, **83**, 596–604.

7. M. Safdarian, P. Hashemi, M. Adeli, *Anal. Chim. Acta,* 2013, **774,** 44– 50.

8. K. Ravindra, L. Bencs, R. V. Grieken, *Sci. Total Environ.,* 2004, **318**, 1–43.

9. K. Mehrani, A. Mehrani, M. M. Amini, O. Sadeghi, N. Tavassoli, *Microchim. Acta,* 2011, **173,** 521–527.

10. Z. Tu, S. Lu, X. Chang, Z. Li, Z. Hu, L. Zhang, H. Tian, *Microchim. Acta,* 2011, **173,** 231–239.

11. P. Liu, Q. Pu, Z. Su, *Analyst*, 2000, **125**, 147–150.

12. P. Kovacheva, R. Djingova, *Anal. Chim. Acta,* 2002, **464**, 7–13.

13. E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, *Microchem. J.,* 2012, **101,** 59–64.

14. E. Yavuz, Ş. Tokalıoğlu, S. Şahan, *J. Braz. Chem. Soc.,* 2013, **24**, 736-742.

15. T. Çetin, Ş. Tokalıoğlu, A. Ülgen, S. Şahan, İ. Özentürk, C. Soykan, *Talanta,* 2013, **105**, 340-346.

16. Ş. Tokalıoğlu, V. Yılmaz, Ş. Kartal, A.Delibaş, C. Soykan, *Microchim. Acta,* 2009, **165**, 347-352.

17. Ş. Tokalıoğlu, T. Oymak, Ş. Kartal, *Anal. Chim. Acta*, 2004, **511,** 255-260.

18. A.M. El-Menshawy, I.M. Kenawy, A.A. El-Asmy, *J. Hazard. Mater.,* 2010, **173**, 523–527.

19. M.H. Mashhadizadeh, Z. Karami, *J. Hazard. Mater.,* 2011, **190**, 1023–1029.

20. B. A. Lesniewska, I. Godlewska, B. G. Zyykiewicz, *Spectrochim. Acta Part B,* 2005, **60**, 377– 384.

21. Q. Liu, J. Shi, G. Jiang, *TrAC, Trends Anal. Chem.,* 2012, **37**, 1-11.

22. T. Hartono, S. Wang, Q. Ma, Z. Zhu, *J. Colloid Interface Sci.*, 2009, **333**, 114–119.

23. E. Zong, D. Wei, H. Wan, S. Zheng, Z. Xu, D. Zhu, *Chem. Eng. J.,* 2013, **221**, 193–203.

24. Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S. M. Shah, X. Su, *J. Colloid Interface Sci.,* 2012, **368**, 540–546.

25. O. G. Apul, Q. Wang, Y. Zhou, T. Karanfil, *Water Res.,* 2013, **47**, 1648-1654.

26. S.-T. Yang, S. Chen, Y. Chang, A. Cao, Y. Liub, H. Wang, *J. Colloid Interface Sci.,* 2011, **359**, 24–29.

27. G. Zhao, T. Wen, X. Yang, S. Yang, J. Liao, J. Hu, D. Shao, X. Wang, *Dalton Trans.,* 2012, **41**, 6182-6188.

28. W. S. Hummers, Jr, R. E. Offeman, *J. Am. Chem. Soc.,* 1958, **80**, 1339.

29. P. Liu, K. Gong, P. Xiao, M. Xiao, *J. Mater. Chem.,* 2000, **10**, 933-935.

30. J. Fang, L.-W. Liu, X.-P. Yan, *Spectrochim. Acta Part B,* 2006, **61**, 864–869.

31. Y. Si, E. T. Samulski, *Nano Lett.*, 2008, **8,** 1679-1682.

32. S. Stankovich, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Carbon*, 2006, **44,** 3342-3347.

33. B. Yang, Q. Gong, L. Zhao, H. Sun, N. Ren, J. Qin, J. Xu, H. Yang, *Desalination,* 2011, **278**, 65-69.

34. Q. He, D. Yang, X. Deng, Q. Wu, R. Li, Y. Zhai, L. Zhang, *Water Res.,* 2013, **47,** 3976-3983.

35. S. Khazaeli, N. Nezamabadi, M. Rabani, H. A. Panahi, *Microchem. J.,* 2013, **106,** 147-153.

36. M.M. Bekheit, N. Nawar, A.W. Addison, D.A. Abdel-Latif, M. Monier, *Int. J. Biol. Macromol.*, 2011, **48**, 558-565.

37. H. Bagheri, A. Afkhami, M.S.-Tehrani, H. Khoshsafar, *Talanta,* 2012, **97**, 87-95.

38. S.Z. Mohammadia, M.A. Karimia, H. Hamidiana, Y.M. Baghelani, L. Karimzadeha, *Sci. Iran,* 2011, **18**, 1636-1642.

39. A. Uheida, M. Iglesias, C. Fontas, M. Hidalgo, V. Salvado, Y. Zhang, M. Muhammed, *J. Colloid Interface Sci.,* 2006, **301**, 402–408.

40. C.Z. Hang, B. Hu, Z.C. Jiang, N. Zhang, *Talanta,* 2007, **71,** 1239–1245.

41. S. Rastegarzadeh, N. Pourreza, A.R. Kiasat, H. Yahyavi, *Microchim. Acta,* 2010, **170**, 135–140.

42. T. Madrakian, A. Afkhami, M. A. Zolfigol, M. Solgi, *J. Hazard. Mater.,* 2006, **128**, 67–72.

43. A. Safavi, N. Iranpoor, N. Saghir, *Sep. Purif. Technol.,* 2004, **40**, 303-308.

44. M. Akhond, G. Absalan, L. Sheikhian, M.M. Eskandari, H. Sharghi, *Sep. Purif. Technol.,* 2006, **52,** 53-59.

<div align="center">**Figure Captions**</div>

Fig. 1. XRD pattern of graphite (a) and graphite oxide (b).

Fig. 2. FTIR spectra of graphite and graphite oxide.

Fig. 3. Effect of the sample pH on the recovery of Ag and Pd.

Fig. 4. Effect of contact time on the adsorption and elution of the Ag and Pd ions.

Fig. 5. Effect of 2,6 diaminopyridine amount on recovery of Ag and Pd.

Fig. 6. Effect of sample volume on the recovery of Ag and Pd.

Fig. 7(a). Linearized Langmuir adsorption of Ag on GO.

Fig. 7(b). Linearized Langmuir adsorption of Pd on GO.
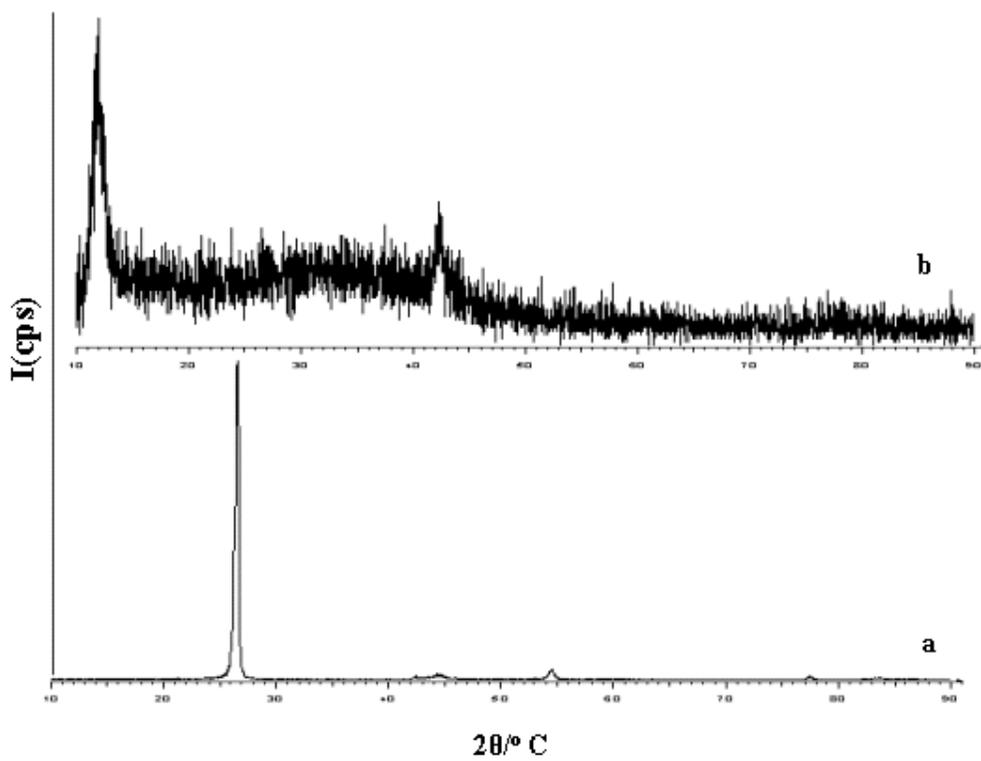
Fig. 1.
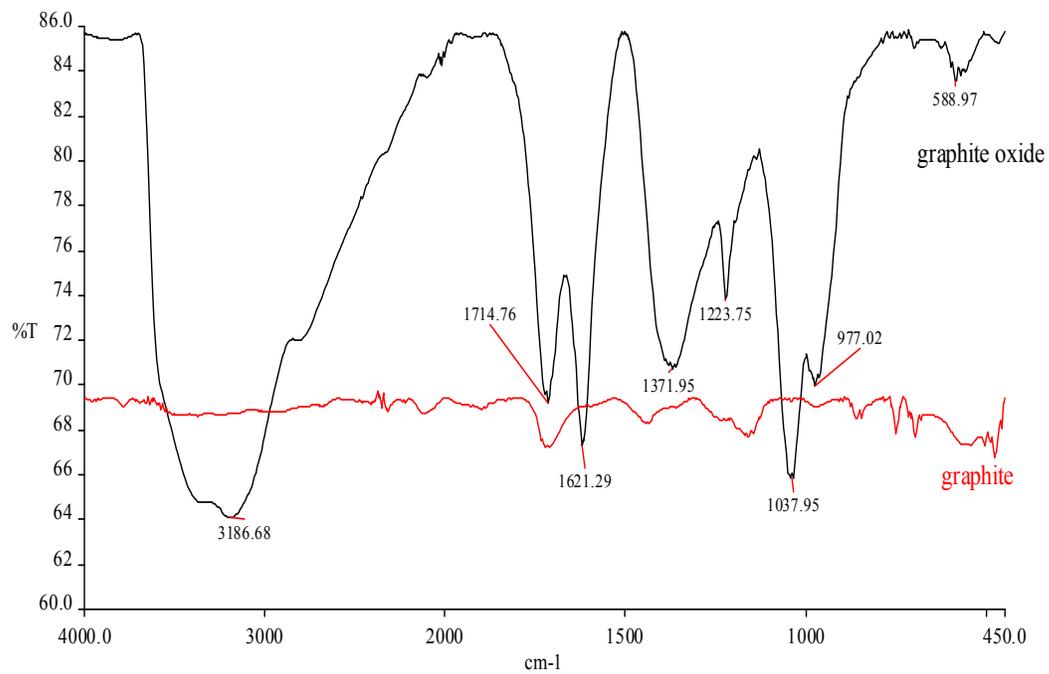
Fig. 2.
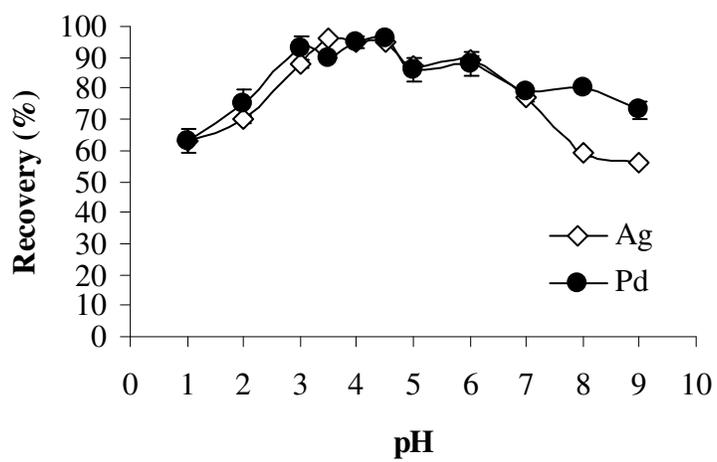
Fig. 3.
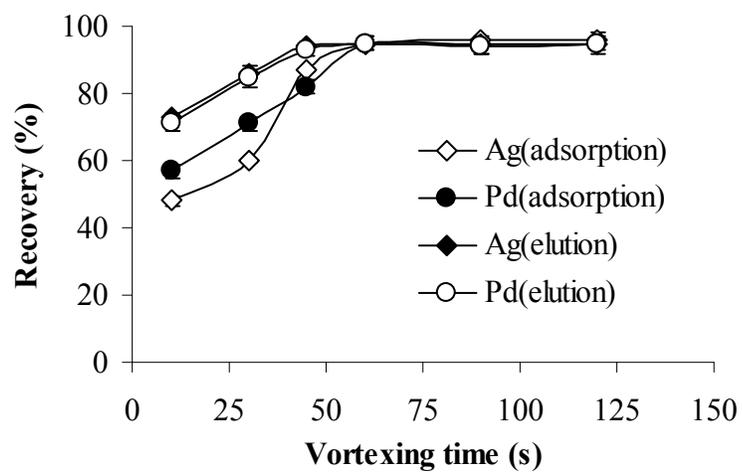
Fig. 4.
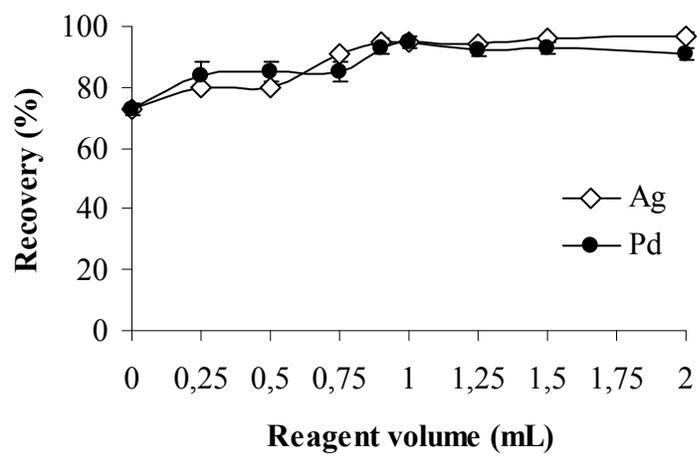
Fig. 5.
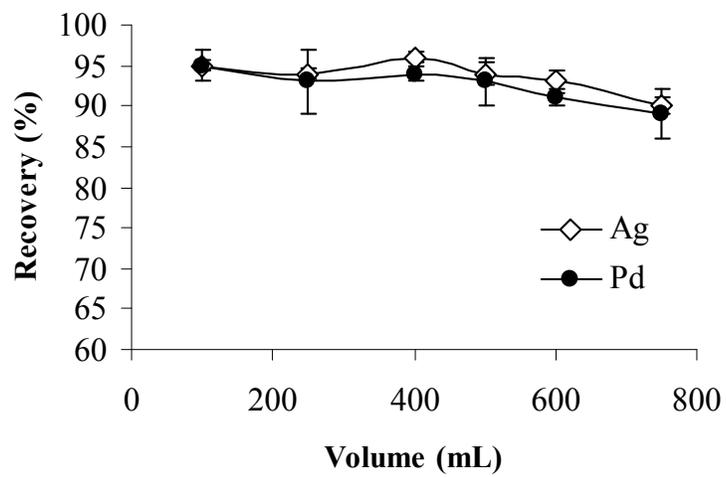
Fig. 6.

Table 1   Effect of concentration of eluents on the recovery of Ag and Pd, eluent volume: 5 mL, n=3

Conc.of HNO_3, (mol L^{-1})	R (%) ± s		Conc. of HCl, (mol L^{-1})	R (%) ± s	
	Ag	Pd		Ag	Pd
1.0	25 ± 1	37 ± 1	1.0	70 ± 1	69 ± 2
1.5	29 ± 1	37 ± 2	1.5	72 ± 1	76 ± 1
2.0	33 ± 2	41 ± 2	2.0	95 ± 1	95 ± 2
3.0	40 ± 1	48 ± 2	3.0	95 ± 1	96 ± 0

Table 2 Tolerance limits of matrix ions on determination of Ag and Pd ions, n=3

Ion	Concentration ($\mu g\ mL^{-1}$)	Salt	Recovery ± s (%)	
			Ag	Pd
Na(I)	1000	NaCl	94 ± 1	90 ± 1
	1500		93 ± 1	94 ± 3
K(I)	1000	KNO_3	98 ± 4	91 ± 2
	1500		93 ± 0	91 ± 0
Mg(II)	1000	$Mg(NO_3)_2.6H_2O$	94 ± 1	95 ± 3
	1500		91 ± 4	92 ± 5
Ca(II)	1000	$Ca(NO_3)_2$	97 ±2	91 ± 2
	1500		92 ± 5	91 ± 4
Fe(III)	25	$Fe(NO_3)_3.\ 9H_2O$	97 ± 2	93 ± 3
Zn(II)	25	$Zn(NO_3)_2.\ 6H_2O$	97 ± 3	97 ± 0
Cu(II)	10	$Cu(NO_3)_2.\ 3H_2O$	94 ± 1	92 ± 1
Al(III)	25	$Al(NO_3)_3.\ 9H_2O$	96 ± 1	93 ± 1
Ni(II)	10	$Ni\ (NO_3)_2.\ 6H_2O$	93 ± 1	92 ± 2
Cd(II)	5	$Cd(NO_3)_2.\ 4H_2O$	96 ± 1	95 ± 2
SO_4^{2-}	100	Na_2SO_4	95 ± 0	92 ± 1
PO_4^{3-}	50	$NaH_2PO_4.2H_2O$	96 ± 1	94 ± 1
Mn(II)	10	$Mn(NO_3)_2.2H_2O$	97 ± 0	89 ±1
Cr(III)	10	$Cr(NO_3)_3.\ 9H_2O$	94 ± 1	93 ± 1
Pb(II)	10	$Pb(NO_3)_2$	95 ± 6	93 ± 1
Au(III)	10	Au standard solution	95 ±1	93 ±1
Co(II)	10	$Co(NO_3)_2.6H_2O$	97 ± 1	89 ± 2

Table 3 Concentrations Ag and Pd in anode slime sample without applying preconcentration method and after applying the method

Ion	Concentration found without applying the method ($\mu g\ g^{-1}$)	Concentration found in eluate after applying the method ($\mu g\ g^{-1}$)
Ca(II)	76 ± 2 [a]	4.4 ± 0.3
Mg(II)	20.6 ± 0.1	1.5 ± 0
Co(II)	120 ± 5	2.3 ± 0
Cu(II)	650 ± 32	81 ± 2
Mn(II)	13 ± 0.3	nd[b]
Fe(III)	$2,606 \pm 99$	142 ± 3
Zn(II)	11.5 ± 0.2	1.5 ± 0
Pb(II)	1.40 ± 0.05	nd
Cr(III)	34 ± 1	1.8 ± 0.3
Cd(II)	nd	nd
Ni(II)	$37,540 \pm 877$	$9,160 \pm 298$
Au(III)	nd	nd
Pd(II)	nd	nd
Ag(I)	nd	22 ± 1

[a] $\bar{x} \pm s$, n=3.
[b] nd: not detected.

Table 4 The analysis results of certified reference materials

Element	TMDA-70 Lake water			[a]SRM 2556 (Used Auto Catalyst Pellets)		
	[b]Certified ($\mu g\ L^{-1}$)	[c]Found ($\mu g\ L^{-1}$)	R(%)	[b]Certified ($\mu g\ g^{-1}$)	[c]Found ($\mu g\ g^{-1}$)	R(%)
Ag	10.9 ± 0.13	$10.6\ \pm 1.0$	97			
Pd				326.0 ± 1.6	330 ± 24	101

[a]The main component of the matrix is Al (40%), Ca (0.1%), Ce (1%), Fe (0.8%), La (0.7%) and Si (0.2%) are present at a relatively high concentration, as well as Ba (100 mg g^{-1}), Zn (600 mg g^{-1}), Zr (300 mg g^{-1}), Pb (6228 mg g^{-1}), Pt (697.4 mg g^{-1}), and Rh (51.2 mg g^{-1}).
[b]At 99 % confidence level.
[c]$\bar{x} \pm s$, n=3.

Table 5 Determination of Ag(I) in water, anode slime and converter samples

Sample	Unit	Added	Found[a]	R(%)
Tap water	$(\mu g\ L^{-1})$	-	0.20 ± 0.03	-
	$(\mu g\ L^{-1})$	10	10.6 ± 0.7	104
	$(\mu g\ L^{-1})$	20	21.0 ± 1.3	104
Mineral water	$(\mu g\ L^{-1})$	-	5.4 ± 0.3	-
	$(\mu g\ L^{-1})$	25	29.5 ± 1.1	97
	$(\mu g\ L^{-1})$	50	53.4 ± 0.4	96
Wastewater	$(\mu g\ L^{-1})$	-	nd[b]	-
	$(\mu g\ L^{-1})$	50	50 ± 3	100
	$(\mu g\ L^{-1})$	100	106 ± 3	106
Anode slime	$(\mu g\ g^{-1})$	-	21.8 ± 0.9	-
	$(\mu g\ g^{-1})$	25	46 ± 3	97
	$(\mu g\ g^{-1})$	50	71 ± 1	99
Converter	$(\mu g\ g^{-1})$	-	162 ± 7	-
	$(\mu g\ g^{-1})$	125	288 ± 11	101
	$(\mu g\ g^{-1})$	250	434 ± 11	109

[a] $\bar{x} \pm s$, n=3.
[b]nd: not detected.

Table 6 Determination of Pd(II) in water, anode slime and catalytic converter samples

Sample	Unit	Added	Found [a]	R (%)
Tap water	(μg L^{-1})	-	5.6 ± 0.1	-
	(μg L^{-1})	20	25.2 ± 2.2	98
	(μg L^{-1})	40	43.6 ± 1.8	95
Mineral water	(μg L^{-1})	-	nd[b]	-
	(μg L^{-1})	50	53 ± 4	106
	(μg L^{-1})	100	107 ± 3	107
Wastewater	(μg L^{-1})	-	nd	-
	(μg L^{-1})	100	109 ± 2	109
	(μg L^{-1})	200	217 ± 18	108
Anode slime	(μg g^{-1})	-	nd	-
	(μg g^{-1})	5	5.2 ± 0.6	104
	(μg g^{-1})	10	10.3 ± 0.9	102
Catalytic converter	(μg g^{-1})	-	728 ± 40	-
	(μg g^{-1})	750	1492 ± 40	102
	(μg g^{-1})	1500	2146 ± 26	95

[a] $\bar{x} \pm s$, n=3.
[b] nd: not detected.

Table 7 Comparison of the published methods with the described method in this work for Ag and Pd preconcentration

Element	Adsorbent/technique	pH	AC[a], (mg g^{-1})	PF[b]	DL[c] (µg L$^-$)	RSD (%)	Adsorption contact time (min)	Reusability	Adsorbent amount (mg)	Sample	Refs
Pd	Activated carbon modified with EAC/ICP-AES	1	92	125	11	2.6	5	10	40	Smelter and road dust	[10]
Pd	Magnetic Fe$_3$O$_4$ nanoparticles/FAAS	10.5	27.2	150	2.9	1.9	2		20	Platinum–iridium alloy, road dust	[38]
Pd	Fe$_3$O$_4$ nanoparticles/ICP-AES	2.5	10.96				30				[39]
Ag, Pd	Nanometer sized alumina modified by QAHBA/ICP-OES	4.5–6.5	5.1, 7.6	10	0.12, 0.44	1.6, 2.3	4	30	50	Certified reference materials,natural water	[40]
Pd	PDR on silica gel-polyethylene glycol/FAAS	1.5	99	125	0.54	2.5-3.8			200	Water, dust, ore	[41]
Ag	2,4,6-trimorpholino-1,3,5-triazin bonded on silica gel/FAAS	3.5	0.384	130		3.03		6	100	Spring, tap water	[42]
Ag	2-mercaptobenzothiazole bonded on silica gel/FAAS	6.2	0.343	300		2.04		4	70	Lake water	[43]
Ag	Di(n-propyl) thiuram disulfide bonded on silica gel/FAAS	5.8	0.330	100	24	1.43			200	Photographic waste, lake water	[44]
Ag, Pd	Graphite oxide-2,6 diaminopyridyne / FAAS	4	1.82, 6.39	120	0.39, 0.94	1.6, 2.5	1	150	100	Tap, mineral, wastewater, anode slime, converter samples	this work

[a] AC: Adsorption capacity. [b] PF: Preconcentration factor. [c] DL: Detection limit. QAHBA: 3-(8-quinolinylazo)-4-hydroxybenzoic acid. PDR: 5(p-dimethylaminobenzylidene)rhodanine. EAC: ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate.

Preconcentration of Ag and Pd ions by using graphite oxide and 2,6 diaminopyridyne from water, anode slime and catalytic converter samples

Gülşen Yıldırım, Şerife Tokalıoğlu, Halil Şahan, Şaban Patat