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Selective solid-phase extraction and separation of trace gold, palladium and platinum using activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate

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Abstract Activated carbon was chemically modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate to obtain a material for selective solid-phase extraction of trace Au(III), Pd(II) and Pt(IV) prior to their determination by inductively coupled plasma atomic emission spectrometry. Experimental conditions such as effects of pH, shaking time, sample flow rate and volume, elution and interfering ions were studied. The ions Au(III), Pd(II) and Pt(IV) can be quantitatively adsorbed on the new sorbent from solution of pH 1. The adsorbed ions were then eluted with 0.1 mol L^{-1} hydrochloric acid and containing 4% thiourea. Many common ions do not interfere. The adsorption capacity of the material is 305, 92, and 126 mg g^{-1} for Au(III), Pd(II) and Pt(IV), respectively, and the detection limits are 5, 11 and 9 ng mL^{-1}. The relative standard deviation is less than 3.0% ($n=8$) under optimum conditions. The method was validated by analyzing two certified reference materials and successfully applied to the preconcentration and determination of these ions in actual samples with satisfactory results.

Keywords Activated carbon · Ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate · Precious metal ions · Solid-phase extractant · Inductively coupled plasma atomic emission spectrometry

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Introduction

Precious metals are widely used in many fields such as catalysts in various chemical processes, electrical and electronic industries, corrosion resistant materials, and jewelry, because of their specific physical and chemical properties [1–3]. Economically, the precious metals have been historically important as currency, and remain important as investment commodities. Gold, silver, platinum and palladium are internationally recognized as forms of currency under ISO 4217 [4]. Along with the usage of these elements, they inevitably entered the environment by various means. For example, the introduction of catalytic converters of automobiles containing platinum, palladium and rhodium (platinum group elements, PGEs) for reducing emission of gaseous pollutants, such as carbon monoxide, nitrogen oxides and hydrocarbons, has resulted in increasing concentration of PGEs in environmental matrices, especially in roadside dust, soil and plants [5–7]. The presence of these elements in such matrices make them potential pollutants [5, 8]. Therefore, the investigation and determination of the precious metals from environment samples became a very important ecological issue.

Sensitive instrumental techniques such as neutron activation analysis (NAA) [9], atomic absorption spectrometry (AAS) [10–15], inductively coupled plasma atomic emission spectrometry (ICP-AES) [16–18], microwave induced plasma atomic emission spectrometry (MIP–AES) [19], inductively coupled plasma mass spectrometry (ICP-MS) [20, 21] and cathodic stripping voltammetry (CSV) [22] have been used for precious metals determination in environmental and biological materials. However, the direct determination by all these techniques is restricted owing to interferences caused by environmental sample matrices. The low concentration of precious metals together with the

high concentration of interfering matrix components in environmental samples often required a preconcentration/ enrichment step combined with a matrix separation.

The most widely used techniques for the separation and preconcentration of trace precious metals include fire assay (FA), coprecipitation, liquid–liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE), solid phase extraction (SPE), dispersive liquid–liquid microextraction (DLLME), big-cycle molecular recognition technology, ion-exchange and sorption, HPLC, and CE [23, 24]. Among these techniques, SPE is preferred on account of the fast, simple and direct application in micro liter volume without any sample loss, higher preconcentration factor, rapid phase separation, time and cost saving [25]. The choice of appropriate sorbent is a critical factor to obtain full recovery and high enrichment factor in SPE procedure. Among the many types of solid phase used in SPE, activated carbon is still by far the most important one because of its large surface area, high adsorption capacity, porous structure, environmentally friendly, low cost and high purity standards [26–28].

In recent years, the development of surface-modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity and selectivity [26]. According to Pearson's hard and soft acid–base theory, polymers containing functional groups with N or O donor atoms should be promising as sorbents of precious metal ions [29, 30]. So, in this work, ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate modified activated carbon (AC-EAC) was synthesized and characterized. The new sorbent showed great affinity, relatively high adsorption capacity and less equilibrium time for Au(III), Pd(II) and Pt(IV). The influences of some analytical parameters on the quantitative recoveries of the analytes were investigated in detail. This method was applied to the preconcentration and determination of trace amount of Au(III), Pd(II) and Pt(IV) from actual samples with satisfactory results.

Experimental

Chemicals and reagents

Unless otherwise stated, all water was double distilled water and all reagents used were of analytical and spectral purity. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to a published procedure [31].

Reagents of high or analytical purity were used for all experiments. 1 mg mL^{-1} Au(III), Pd(II) and Pt(IV) standard stock solutions were prepared by dissolving spectroscopically pure HAuCl$_4$·4H$_2$O, PdCl$_2$ and (NH$_4$)$_2$PtCl$_6$ in dilute HCl, respectively. Working standard solutions were made by

diluting the standard stock solution with 0.5 mol L^{-1} HCl. Activated carbon (AC), gas chromatographic grade, 100–200 mesh (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China, http://www.guangfu-chem.com), ethylenediamine (EDA) (The First Reagent Factory, Shanghai, China, http://www.reagent.com.cn), pyridine (The First Reagent Factory, Shanghai, China, http://www.reagent.com.cn) and ethyl-2-chloroacetoacetate (A Johnson Matthey Company, Tianjin, China, http://www.alfa.com) were used in this work. N,N′-dicyclohexylcarbodiimide (DCC) was purchased from Sinopharm Chemical Co. Ltd (Shanghai, China).

Instruments and apparatus

An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (Thermo Jarrel Ash, Franklin, MA, USA, http://www.thermo.com) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected were as follows: Au(III) 242.795 nm, Pd(II) 360.955 nm, Pt(IV) 214.423 nm. A pHs-3C digital pH meter (Shanghai Lei Ci Device Works, Shanghai, China, http://www.lei-ci.com) was used for the pH adjustments. Infrared spectra (4000–400 cm^{-1}) in KBr were recorded on a Nicolet NEXUS 670 FT-IR spectrometer (Nicolet, Madison, WI, USA, http://www.thermo.com). A VarioEL element analyzer (Hanau Germany) was used for elemental analysis. Photoelectron spectroscopy analyses was carried out on a PHI-5702 Photoelectron Spectroscopy (American Physical Electron Company, USA). An YL-110 peristaltic pump (General Research Institute for Non-ferrous Metals, Beijing, China, http://www.grinm.com) was used in the column process. A PTFE (polytetrafluoroethylene) column (45 × 3.0 mm i.d, Tianjin Jinteng Instrument Factory, Tianjin, China) was used.

Sample preparation

The geological-certified reference material (GBW07293, platinpalladium ore) was purchased from the Institute of Geophysical and Geochemical Prospecting for Certified Reference Materials (Langfang, China, http://www.lfbohai.cn). A 1.0000 g accurately weighed amount of GBW07293 (dried at 100°C for 4 h) and 1.0 g of sodium peroxide were weighed in nickel crucibles and placed in a muffle furnace for 15 min at 700°C. The residues were dissolved in hot water in a beaker and solutions obtained were heated to near dryness. Then, the residues were dissolved in dilute hydrochloric acid and the dissolved salts were then centrifuged [17]. Before use, the pH value was adjusted to 1 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} ammonia solution.

For the auto catalyst NIST SRM 2557 reference material (National Institute of Standards and Technology, Gaithersburg, USA, http://www.nist.gov), 0.0500 g of this

reference material was weighed and dissolved in 5 mL of HNO_3–$HClO_4$–HF (4:2:1 v/v/v) under mild heating and vaporized to near dryness. Then 5 mL aqua regia was added to the residue and the solution was evaporated carefully again to dryness, and finally dissolved in 5 mL of 0.5 mol L^{-1} nitric acid [23].
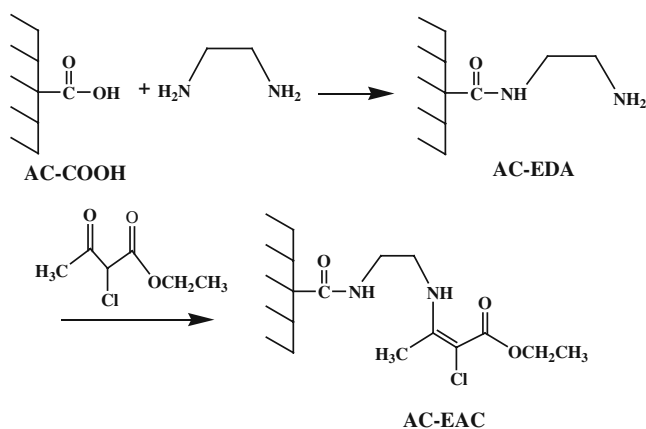
Road dust was collected from Tianshui Road, Lanzhou, China. 1.0000 g of road dust was weighed and dissolved in 20 mL of HNO_3–$HClO_4$–HF (4:2:1 v/v/v) under mild heating and vaporized to near dryness. Then 10 mL aqua regia was added to the residue and the solution was evaporated carefully again to dryness, and finally dissolved in 10 mL of 0.5 mol L^{-1} nitric acid.

Smelter sample was obtained from Jinchuan Company, Lanzhou, China. The sample (0.2000 g) was added to a nickel crucible containing a 0.5 g Na_2CO_3 and 1.5 g Na_2O_2 mixture, and was covered with a little amount of Na_2CO_3–Na_2O_2 mixture. The sample was then fused in an electric muffle at 700°C for 10 min. After cooling, it was dissolved in hot water and transferred into a beaker. Concentrated HCl was added to adjust the acidity. The solution was boiled for 30 min, and then filtered. The residue and filter paper were washed with 2.0 mol L^{-1} HC1 several times [32]. Then the solution was filtered into a 100 mL calibrated flask.

Preparation of new sorbent

Preparation of AC-EAC

Activated carbon powder was first treated with 10% (v/v) hydrochloric acid solution for 24 h so as to remove the metal ions and other impurities sorbed on it. Then 10 g of treated activated carbon was suspended in 300 mL of 5.0 mol L^{-1} nitric acid solution under stirring and heating for 5 h at 60°C. The mixture was filtered and washed with deionized water to neutral and dried under vacuum at 80°C

for 8 h. The product was carboxylic derivative of activated carbon (AC-COOH).

Activated carbon-bound ethylenediamin (AC-EDA) was synthesized according to the following procedure. A 5.0 g amount of AC-COOH was suspended in 150 mL of ethylenediamine under stirring and heating, then 5.0 g of N,N′-dicyclohexylcarbodiimide (DCC) was added into the suspension as a dehydrating agent and refluxed for 48 h [26]. The product (AC-EDA) was filtered off, washed with ethanol and dried under vacuum at 80°C for 8 h.

For the synthesis of ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate modified activated carbon (AC-EAC), 4.5 g AC-EDA, 6.2 g ethyl-2-chloroacetoacetate, 25 mL dry ethanol and 3 mL pyridine were added to a 100 mL round flask equipped with a magnetic stirrer. The mixture was stirred for 5 h at room temperature, and then refluxed for 12 h [33]. The product (AC-EAC) was filtered off, washed with ethanol and dried under vacuum at 80°C for 8 h. The synthetic route of AC-EAC is illustrated in Scheme 1.

Characterization of AC-EAC

FT-IR spectra were taken by using KBr to observe the functional groups of AC-COOH and AC-EAC and the spectra were shown in Fig. 1. According to the literature [34, 35], the peaks can be assigned as follows: the bands of AC-COOH at 1706 cm^{-1} was assigned to free carboxylic acid absorptions. The band at 3398 cm^{-1} could be assigned to the stretching vibration of N–H and O–H. The peaks of 2921 cm^{-1} and 2852 cm^{-1} were due to C–H stretching
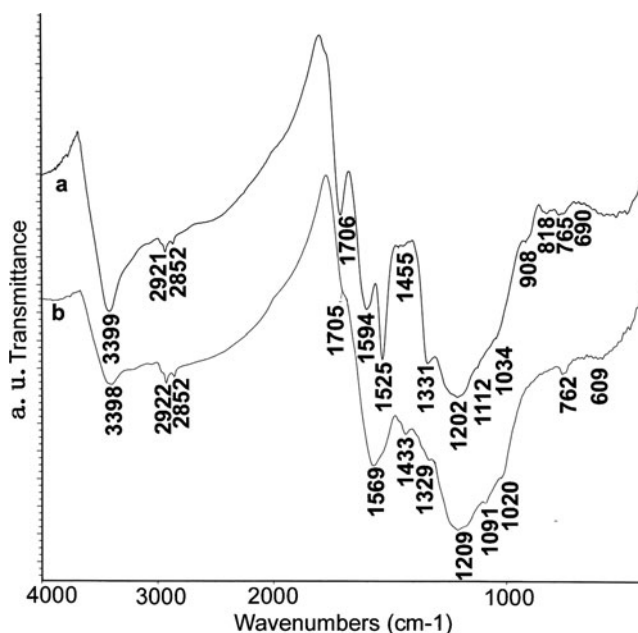

Scheme 1 Synthetic route of the AC-EAC

Fig. 1 IR spectra of AC-COOH (**a**) and AC-EAC (**b**)

vibration. The bands observed at 1594 cm^{-1}, 1525 cm^{-1} and 1455 cm^{-1} could be assigned to C=C stretching vibration. Peaks of 690–1200 cm^{-1} were ascribed to the bending vibration of N–H. Comparison of the IR spectrum of AC-EAC with AC-COOH, the new peak at 1569 cm^{-1} resulted from C=C stretching vibration and bending vibration of N–H. The peaks at 1091 cm^{-1} and 1020 cm^{-1} were due to C–N stretching vibration. The bands around 1209 cm^{-1} could be assigned to C–O–C stretching vibration. The peaks of 609 cm^{-1} and 762 cm^{-1} could be assigned to the stretching vibration of C–Cl.

Elemental analysis indicated that the content of carbon, nitrogen and hydrogen for AC-COOH and AC-EAC was 60.07% and 70.80%, 2.80% and 8.69%, 2.95% and 3.18% respectively. Higher carbon and nitrogen content was observed in AC-EAC, they were also consistent with above FT-IR analysis results.

Photoelectron spectroscopy analyses results showed that the molar percentages of carbon, nitrogen, oxygen and chlorine for AC-COOH and AC-EAC was 75.75% and 77.98%, 3.91% and 6.73%, 20.34% and 14.76%, 0 and 0.53%. Photoelectron spectroscopy of Cl2p in AC-EAC was shown in Fig. 2.

Consequently, the above experimental results suggest that activated carbon is successfully modified by ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate.

Procedures

Batch method

A series of standard or sample solutions containing Au(III), Pd(II) and Pt(IV) were transferred into a 25 mL beaker, and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl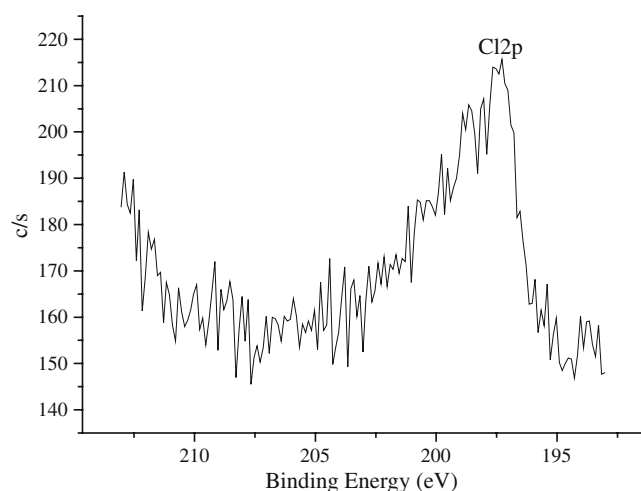 and 0.1 mol L^{-1} ammonia solution. Then the volume was adjusted to 10 mL using double distilled water. 40 mg of AC-EAC was added, and the mixture was shaken vigorously for 20 min to facilitate adsorption of the metal ions onto the sorbent. After centrifugation, the concentrations of the metal ions in the solution were determined by ICP-AES.

Column SPE procedure

A 40 mg of functionalized activated carbon adsorbent was packed in the PTFE column plugged with a small portion of glass wool at both ends. After cleaning by passing through ethanol and double distilled water once more, the column was conditioned to the desired pH with 0.1 mol L^{-1} HCl. Portions of aqueous standard or sample solutions containing Au(III), Pd(II) and Pt(IV) were passed through the column at a flow rate of 2.5 mL min^{-1} after adjusting to the desired pH. Afterwards, the metal ions retained on column were eluted with 0.1 mol L^{-1} HCl and 4% (m/v) thiourea solution and the analytes in the eluate were determined by ICP-AES.

Results and discussion

Effect of pH

Among the studied chemical variables affecting the adsorption process, pH is one of the most important factors. According to the recommended procedure (batch method), the effect of pH on the adsorption of Au(III), Pd(II) and Pt(IV) was tested and determined by equilibrating 40 mg AC-EAC with 10 mL 1.0 μg mL^{-1} of Au(III), Pd(II) and Pt(IV) at different pH value, namely pH 1, 2, 3, 4, 5, 6 and 7. It could be seen in Fig. 3 that the optimum pH for quantitative extraction (>95%) of Au(III), Pd(II) and Pt(IV) occurred at pH 1–6. At higher pH, fewer recoveries were seen. At the same time, activated carbon without any modification were
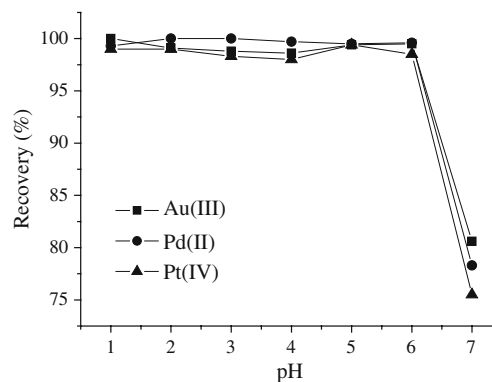

Fig. 2 Photoelectron spectroscopy of Cl2p in AC-EAC

Fig. 3 Effect of pH on adsorption of 1.0 μg mL^{-1} Au(III), Pd(II) and Pt(IV) on AC-EAC. Other conditions: shaking time 30 min, temperature 25°C

tested by the same experiments, we found that these ions had insignificant adsorption on unmodified activated carbon. Au(III), Pd(II) and Pt(IV) adsorption on the AC-EAC may be due to ionic interaction mechanism between protonated amines and chloro-anionic metal complexes, chelation of Au(III), Pd(II) and Pt(IV) and N or O donor atoms on the AC-EAC or both two mechanisms [4, 30, 36]. Amino AC-EAC can be protonated at acidic conditions. Ionic interaction is very effective in the adsorption of Au(III), Pd(II) and Pt(IV). Oxygen atoms may also contribute to the adsorption because of hard/soft acid/base theory by Pearson [29]. At low pH, when the solution pH was controlled by HCl, the amount of chloride in the solution is high enough to favor the formation of chloro-anionic spices that will be adsorbed on protonated amine groups of AC-EAC. At higher pH, the decreased adsorption of precious metals may be explained by the presence of less-adsorbable Au(III), Pd(II) and Pt(IV) species because of the lower availability of chloride anions [4]. In order to eliminate the adsorption of other metal ions, the optimum acidity was selected as pH 1. The later experimental studies were carried out after acidity of feed solutions was adjusted as pH 1.

In addition, 1.0 μg mL^{-1} of Ru(IV), Rh(III), Ir(IV), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) was also tested by the same experiments at pH 1. The results showed that Ru(IV), Rh(III), Cr(III), Fe(III), Co(II), Ni(II) and Zn(II) were not enriched by AC-EAC at pH 1; Cd(II), Pb(II), Cu(II) and Ir(IV) could be adsorbed by AC-EAC about 10–40% at pH 1, but they do not interfere with enrichment and determination of Au(III), Pd(II) and Pt(IV). The results suggested that AC-EAC had high selectivity for Au(III), Pd(II) and Pt(IV).

Effect of shaking time

The effect of shaking time is another important factor in evaluating the affinity of AC-EAC to ions. To determine the rate of loading of Au(III), Pd(II) and Pt(IV) on the AC-EAC, the recommended batch procedure was carried out. In this work, different shaking time (ranged from 2 to 30 min) was studied for the percentage extraction of Au(III), Pd(II) and Pt(IV) by AC-EAC. The results showed that the adsorption of Au(III), Pd(II) and Pt(IV) was over 95% sorption during the first 5 min, which indicated that kinetics of adsorption equilibrium was very fast.

The optimization of elution conditions

It was found that Au(III), Pd(II) and Pt(IV) could not be eluted by HCl solution without thiourea. Hence, a mixed solution of HCl and thiourea was used for fast and quantitative desorption of the retained analytes from the column.

Concentration of thiourea

By keeping the concentration of HCl at 1.0 mol L^{-1}, the effect of thiourea concentration on the desorption of the studied ions was investigated with the thiourea concentration varying among 1–5% (m/v). The results showed that the recovery of Au(III), Pd(II) and Pt(IV) increased with the increase in concentration of thiourea first and then remained constant with further increase in thiourea concentration. Considering the possible effect of thiourea on the subsequent ICP-AES determination, 4% (m/v) thiourea was chosen in this work.

Concentration of HCl

By keeping the thiourea concentration at 4%, the effect of HCl concentration on the desorption of analytes was explored. It was found that Au(III), Pd(II) and Pt(IV) can be easily eluted with the HCl concentration of 0.1 mol L^{-1}. In this work, 0.1 mol L^{-1} HCl was selected.

Elution volume and elution flow rate

The effect of elution volume for quantitative elution of the studied ions was investigated. It was found that 2.0 mL of elution solution containing 0.1 mol L^{-1} HCl and 4% (m/v) thiourea was sufficient to recover analytes quantitatively. The effect of elution flow rate on recovery of analytes was investigated by keeping the elution volume of 2.0 mL. The result indicates that the analytes can be recovered quantitatively in flow rate range of 0.5–2.0 mL min^{-1}. Hence, elution flow rate of 2.0 mL min^{-1} was selected in this experiment.

Effect of sample flow rate

In an SPE system, the flow rate of sample solution not only affects the recoveries of analytes, but also controls the analysis time. Therefore, the effect of the flow rate of
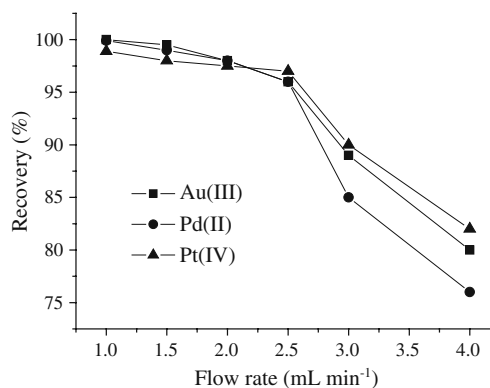

Fig. 4 Effect of solution flow rates on adsorption of 1.0 μg mL^{-1} Au(III), Pd(II) and Pt(IV) on AC-EAC. Other conditions: 40 mg of AC-EAC, volume 10 mL, pH 1, temperature 25°C

Table 1 Effect of potentially interfering ions on percent recovery of 1.0 µg mL^{-1} Au(III), Pd(II) and Pt(IV) on the sorbent followed by elution with 2.0 mL 0.1 mol L^{-1} HCl and 4% (m/v) thiourea

Coexisting ions	Concentration (µg mL^{-1})	Recovery of analytes (%)		
		Au(III)	Pd(II)	Pt(IV)
K$^+$	2000	99.4	95.5	96.2
Na$^+$	2000	98.7	96.4	96.8
Cl$^-$	2000	97.9	98.1	95.6
Ca^{2+}	1000	99.1	96.1	97.4
Mg^{2+}	1000	96.4	95.7	98.4
SO$_4^{2-}$	1000	96.5	96.4	99.6
H$_2$PO$_4^-$	500	97.7	98.6	97.5
Ru(IV)	100	98.0	99.3	98.7
Rh(III)	100	97.5	98.6	95.6
Cr(III)	100	96.5	98.6	98.6
Fe(III)	100	98.7	97.6	95.7
Co(II)	100	96.4	95.9	96.4
Ni(II)	100	99.5	96.3	96.5
Cu(II)	100	96.5	96.8	97.6
Zn(II)	100	99.1	96.4	97.8
Cd(II)	100	98.6	95.6	98.7
Pb(II)	100	97.9	98.4	98.4
Ir(IV)	50	96.4	99.2	96.6

sample solution was examined under the optimum conditions by passing 10 mL of sample solution through the microcolumn with a peristaltic pump. The flow rates were adjusted in range of 1.0–4.0 mL min^{-1}. As shown in Fig. 4, it was found that the the studied ions could be sorbed quantitatively from the adsorbent at flow rates of 1.0–2.5 mL min^{-1}. The recovery of the analytes decreased slightly and could not be adsorbed sufficiently when the flow rate was over 2.5 mL min^{-1}. Thus, sample flow rate of 2.5 mL min^{-1} was employed in this work.

Maximum sample volume and enrichment factor

The enrichment factor was studied by the recommended column procedure. An increasing volume of sample solutions containing 5.0 µg Au(III), Pd(II) and Pt(IV) was passed through the column with the optimum flow rate. Quantitative recovery (>95%) of the Au(III), Pd(II) and Pt (IV) was obtained for the sample volume of 250 mL and at greater volume percent of recovery decreased. Therefore, 250 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. The adsorbed metal ions could be eluted with 2.0 mL of 0.1 mol L^{-1} HCl and 4% (m/v) thiourea solution, so the enrichment factor achieved by this method was 125.

Adsorption capacities

The adsorption capacity is an important factor because it determines how much sorbent is required to quantitatively

concentrate the analytes from a given solution. The adsorption capacity was tested following the batch procedure. 20 mg of sorbent was equilibrated with 10 mL of various concentrations of Au(III), Pd(II) and Pt(IV) for 24 h at pH 1 at 25°C. In order to reach the "saturation", the

Table 2 Analytical results for the determination of actual samples

Sample	Added (µg g^{-1})	Found[a] (µg g^{-1})	Recovery (%)
Smelter sample			
Au(III)	0	19.8±3.6	–
	5	24.0±2.1	96.8
	10	29.9±4.9	100.3
Pd(II)	0	42.7±3.7	–
	5	47.1±3.5	98.7
	10	51.9±5.8	98.5
Pt(IV)	0	30.5±5.5	–
	5	34.5±1.7	97.2
	10	39.3±1.5	97.0
Road dust			
Au(III)	0	n.f.[b]	–
	0.5	0.510±0.040	102.0
Pd(II)	0	0.011±0.009	–
	0.5	0.506±0.020	99.0
Pt(IV)	0	0.027±0.005	–
	0.5	0.520±0.070	98.7

[a] The value following "±" is the standard deviation (n=5)

[b] n.f., not be found

Table 3 Analytical results of Au(III), Pd(II) and Pt(IV) in GBW07293 geological reference material and Pd(II) and Pt(IV) in auto catalyst NIST SRM 2557 reference material

Sample		Found[a] ($\mu g\ g^{-1}$)	Certified value ($\mu g\ g^{-1}$)
GBW07293	Au(III)	0.042±0.005	0.045±0.002
	Pd(II)	0.565±0.090	0.568±0.051
	Pt(IV)	0.410±0.060	0.440±0.036
NIST SRM 2557	Pd(II)	232±5	233±18
	Pt(IV)	1129±11	1131±11

[a] $\overline{x} \pm s$ ($n=5$). $\overline{x}$ average value for five determinations, s standard deviation

initial metal ions, concentrations were increased till the plateau values (adsorption capacity values) obtained. The sorption capacities of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the ligand immobilized onto matrix. From the experimental data, the maximum adsorption capacity of AC-EAC for Au(III), Pd(II) and Pt(IV) was found to be 305, 92 and 126 mg g^{-1}, respectively.

Stability tests

To test the stability and potential reusability of the column, several loading and elution operations cycles were carried out. The operating capacity was calculated from the loading and elution tests. The results from three tests yielded <5% error up to 10 cycles of repeated experiments. The adsorbent showed better reusability and stability towards Au(III), Pd(II) and Pt(IV).

Interference studies

In order to assess the possible analytical applications of the procedure presented, the effect of some potentially interfering ions which may be interfere with the method or/and often accompany analyte ions in various real samples was examined under the optimized conditions at above. For these studies, solutions of 1.0 $\mu g\ mL^{-1}$ of Au(III), Pd(II) and Pt(IV) containing the added interfering ions were treated according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 95%. The results given in Table 1 showed that the presence of major coexisting ions has no obvious influence on the determination of Au(III), Pd(II) and Pt(IV) under the selected conditions, indicating that the present AC-EAC has a potential to be applied to analyze real sample.

Analytical precision and detection limits

Under the selected conditions, eight portions of mixed standard solutions were enriched and analyzed simultaneously by following the recommended procedure. The relative standard deviation (RSD) of the eight replicate determinations was lower than 3.0% (Au(III): 2.6%; Pd(II): 1.9%; Pt(IV): 2.3%). It indicates that the method has good precision for the analysis of trace Au(III), Pd(II) and Pt(IV) from solution

Table 4 Comparison of capacities

Adsorbent	Adsorption capacity (mg/g)			Ref.
	Au(III)	Pd(II)	Pt(IV)	
3-(8-Quinolinylazo)-4-hydroxybenzoic acid modified nanometer-sized alumina	17.7	7.6		[17]
(E,E,E)-1-[(4-methylphenyl)sulfonyl]-6-[(2-trimethylsilylethyl)sulfonyl]-11-[(4-vinylphenyl) sulfonyl)]-1,6,11-triazacyclopentadeca-3,8,13-triene functionalized polystyrene		38.31	54.62	[29]
Nanometer TiO$_2$ immobilized on silica gel	3.56			[37]
Fe$_3$O$_4$ nano-particles		10.959	13.266	[38]
Bayberry tannin immobilized collagen fiber membrane		33.4	45.8	[39]
Amberlite XAD-2000/DDTC	12.3			[40]
Amberlite IRC 718	135.93	58.52	66.334	[41]
Amidinothioureido-silica gel	54.56	15		[10]
2-Mercaptobenzothiazole-bonded silica gel	4.5	18	6.5	[42]
Ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate modified activated carbon	305	92	126	This work

samples. According to the definition of IUPAC, the detection limit of the method was calculated based on three times the standard deviation of eight runs of the blank solution, the detection limits of this method for Au(III), Pd(II) and Pt(IV) were found to be 5, 11 and 9 ng mL^{-1}, respectively.

Application of the method

This method was applied to the determination of analytes in a smelter sample and road dust sample, and the analytical results were given in Table 2. For the analysis of the two actual samples, the standard addition method was used. The recoveries of analytes were in range of 96.8–102%.

In order to establish the validity of the procedure, the method had been applied to the determination of the content of Au(III), Pd(II) and Pt(IV) in geological standard reference material (GBW07293, platinpalladium ore), and Pd(II) and Pt (IV) in auto catalyst NIST SRM 2557 reference material. The results were listed in Table 3. As could be seen, a good agreement was obtained between the determined and certified values.

Comparison with other methods

Table 4 compares the adsorption capacity of different types of adsorbents [37–42] for Au(III), Pd(II) and Pt(IV) adsorption. The adsorption capacity of AC-EAC was relatively high when compared to several other adsorbents. The differences of precious metal ion uptake on various adsorbents are due to the properties (function groups, surface area, particle size, etc.) of the adsorbents [4]. In addition, the enrichment factor achieved by this method is superior to some other reported methods [2, 8, 13, 14, 17, 23, 29]. We can also find lower detection limits when compared with previously reported methods [10, 40].

Conclusions

In conclusion, we have developed a simple, convenient, rapid, sensitive and reliable method for determination of trace level of Au(III), Pd(II) and Pt(IV) in aqueous solution based on activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate as a solid phase extractant. This new adsorbent exhibited good characteristics for separation and preconcentration of Au(III), Pd(II) and Pt(IV) in aqueous solution, such as excellent selectivity, fast adsorption equilibrium, high tolerance limits of potentially interfering ions, high enrichment factor and low costs. It also shows relatively high adsorption capacity when compared to several other adsorbents. In addition, the synthetic method of the adsorbent was very simple. Moreover, the reliable method has been successfully applied to the analysis of trace Au(III), Pd(II)

and Pt(IV) in certified and actual samples with satisfactory results. So, we have demonstrated that the new adsorbent has high analytical potential for analysis of trace Au(III), Pd(II) and Pt(IV) from environmental samples.

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