

Modified Activated Carbon as Selective Solid-Phase Extractant Used for Determination of Au(III), Pd(II) and Pt(IV) by ICP-OES

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A new solid-phase extractant was synthesized by immobilizing N-aminopropyl-(3,4,5-trihydroxy)benzamide on activated carbon for separation/preconcentration trace of Au(III), Pd(II) and Pt(IV) ions prior to the measurement by inductively coupled plasma optical emission spectrometry (ICP-OES). Different variables that can affect the adsorption of Au(III), Pd(II) and Pt(IV) were optimized including acidity, sample flow rate, volume, elution conditions and potentially interfering ions. The optimal pH value was 2. The adsorption capacity of the material was 195.7, 95.1 and 99.3 mg g⁻¹ for Au(III), Pd(II) and Pt(IV), respectively. Then the adsorbed ions were quantitatively eluted by 4 mL of 3 mol L⁻¹ HCl-6 % CS(NH₂)₂ solution. The presence of several interfering ions, which existed in high excess, did not interfere in both separation and determination of the noble ions. The detection limit of the method (3σ) was 7, 11 and 6 ng mL⁻¹ for Au(III), Pd(II) and Pt(IV), respectively. The relative standard deviation (RSD) in optimum conditions was less than 3 % (n = 11). The developed method has been successfully applied to the preconcentration and determination of Au(III), Pd(II) and Pt(IV) in actual samples.

Keywords: Solid-phase extraction, Au(III), Pd(II), Pt(IV), Activated carbon, ICP-OES.

INTRODUCTION

Noble metals are widely used in modern industry because of their specific physical and chemical properties¹⁻³. A small part of the noble metal in catalyst of vehicle exhaust treatment device will be released into the environment. With the significant growth of automotive family, it is inevitable that amounts of noble metals releasing into the atmosphere and causing harm to humans and animals. Unfortunately, the content of noble metals in the earth's crust is very low. Therefore, it is very important to analyze the provision of them accurately and effectively.

Some analytical techniques such as flame atomic absorption spectrometry (FAAS)⁴, polarography and voltammetry analysis⁵, inductively coupled plasma optical emission spectrometry (ICP-OES)⁶, chemiluminescence analysis⁷ and inductively coupled plasma mass spectrometry (ICP-MS)⁸ were generally used in the determination of trace metal ions. Inductively coupled plasma optical emission spectrometry is accepted as the most popular method because of its advantages of simplicity, rapid simultaneous multi-element analysis, low matrix effects and good precision. However, the direct measurement for trace noble metal ions is difficult because of their low concentrations and matrix effects in environmental matrices. Therefore, a sample separation/preconcentration step prior to

analysis is necessary. Most of the reported methodologies for separation and preconcentration involve liquid-liquid extraction (LLE)⁹, cloud point extraction (CPE)¹⁰, electro-deposition¹¹ and solid-phase extraction (SPE)⁶. Among these procedures, the solid phase extraction is the most effective method owing to its advantages of simplicity, low consumption of samples and higher enrichment factor.

So far, it is reported that many adsorbents such as zeolites¹², polymeric materials¹³, *etc.* have been used in solid-phase extraction. In particular, activated carbon is the most widely used matrixes due to its large surface area, high adsorption capacity, porous structure and durability. However, pristine activated carbon possesses relatively poor adsorption selectivity. The development of surface-modified method has generated a diversity of activated carbon with the superior adsorption capacity and selectivity¹⁴. Organically modified activated carbon is mainly used for adsorbing lead¹⁵, mercury¹⁶ and other common metal ions contamination because the existences of the heteroatom such as oxygen, nitrogen, sulfur¹⁷ and phosphorus on its surface. To the best of our knowledge, the adsorption of noble metals has little reported so far.

Hereby, in this work, N-aminopropyl-(3,4,5-trihydroxy) benzamide modified activated carbon (AC-ATB) was synthesized and characterized by FT-IR, elemental analysis and SEM

analysis. A new rapid and selective method for preconcentration and determination of trace Au(III), Pd(II) and Pt(IV) ions was established. Common coexisting ions did not interfere with the determination of target ions. The method was successfully applied to the preconcentration and determination of trace Au(III), Pd(II) and Pt(IV) ions from actual sample.

EXPERIMENTAL

All metal ions were determined by IRIS Advantage ER/S inductively coupled plasma emission spectrometer (Thermo Jarrel Ash, Franklin, MA, USA). The main parameters of ICP-OES (r.f. Power: 1.15 kw; carrier gas (Ar) flow rate: 0.6 L min⁻¹; auxiliary gas (Ar) flow rate: 1 L min⁻¹; coolant gas (Ar) flow rate: 14 L min⁻¹; nebulizer flow: 30 psi; pump rate: 100 rpm; observation height: 15mm; integration time on-axis/off-axis: 20/5 s; the wavelengths selected were as follow: 242.795 nm for Au(III), 360.955 nm for Pd(II) and 214.423 nm for Pt(IV)).

The pH adjustment was controlled with a pHs-3C digital pH meter (Shanghai LeiCi Device Works, Shanghai, China). Fourier Transform Infrared (FT-IR) spectra (4000-200 cm⁻¹) were recorded on a Nicolet Nexus 670 FT-IR spectrometer (Nicolet, Madison, WI, USA). A Vario EL element analyzer named Elementar Analysen systeme (Hanau, Germany) was used for elemental analysis. The scanning electron microscope (SEM) used was Model JSM-6701F by JEOL, Tokyo, Japan. Home-made glass micro-columns (50 mm × 2.5 mm i.d.) were used in this study.

Unless otherwise stated, all chemicals used were of analytical grade and all solutions were prepared with doubly distilled deionized water. Standard labware and glassware used were repeatedly cleansed with HNO₃ and rinsed with double distilled water prior to use, in accordance with a published program¹⁸. Standard stock solutions of Au(III), Pd(II) and Pt(IV) (1 mg mL⁻¹) were prepared by dissolving spectral pure grade chemicals HAuCl₄·4H₂O, PdCl₂ and (NH₄)₂PtCl₆ (Shanghai Reagent Factory, Shanghai, China) in hydrochloric acid (The First Reagent Factory, Shanghai, China) with the addition of doubly distilled water.

Activated carbon (AC, gas chromatographic grade, 100-200 mesh) and gallic acid monohydrate were obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). *N,N'*-dicyclohexyl carbodiimide (DCC) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and ethylenediamine (EDA) was obtained from The First Reagent Factory (Shanghai, China).

Sample preparation: The reference materials (GBW07808, GBW07293) were obtained from National Research Center for Certified Reference Materials (Beijing, China). Alloy sample was obtained from Jinchuan Group Ltd. Sample preparation was based on the literatures^{19,20}. 0.1000 g accurately weighed amount of alloy sample was fused with 0.3000 g of Na₂CO₃ and 0.8000 g of Na₂O₂ in a 10 mL porcelain crucible and heated to 700 °C in a muffle furnace for 15 min. After cooling, the sample was leached with boiling distilled water and transferred into a beaker. 10 mL of concentrated hydrochloric acid was added to the beaker. The mixture was boiled for 45 min and then filtered. The solution was diluted to a 100 mL volumetric flask and made up to volume with double distilled water.

Preparation of new sorbent: In order to remove adsorbed impurities, activated carbon powder was first purified with hydrochloric acid solution (15 % v/v) for 36 h. Then 10 g of purified activated carbon was immersed in 200 mL 30 % (v/v) nitric acid solution and heated for 6 h at 65 °C in order to increase the number of oxygen functional groups on the surface and improve the adsorbing process. The mixture was filtered, washed with deionized water until it was free from acid and dried under vacuum at 85 °C for 10 h and then the carboxylic derivative of activated carbon (AC-COOH) was obtained.

5 g of AC-COOH was suspended in 150 mL of ethylenediamine under stirring and then 5 g of *N,N'*-dicyclohexyl carbodiimide (DCC) was added into the suspension and refluxed at 120 °C for 48 h²¹. The mixture was filtered off, washed with ethanol and dried in a vacuum oven at 80 °C for 8 h. Thus, the activated carbon-bound ethylenediamine (AC-EDA) was obtained.

For the synthesis of *N*-aminopropyl-(3,4,5-trihydroxy) benzamide modified activated carbon (AC-ATB). AC-EDA (4.5 g) and gallic acid (8 g) were suspended in 80 mL of ethanol. This mixture was refluxed at 80 °C for 48 h with the DCC in tetrahydrofuran solution slowly added. The final product (AC-ATB) was filtered, washed with toluene, dimethyl-formamide and methanol several times and then dried under vacuum at 75 °C for 6 h. The synthetic route of AC-ATB is illustrated in Fig. 1.

Procedure

Batch procedure: A series of standards or sample solutions containing Au(III), Pd(II) and Pt(IV) were adjusted the pH to the desired value. Then the volume was adjusted to 10 mL

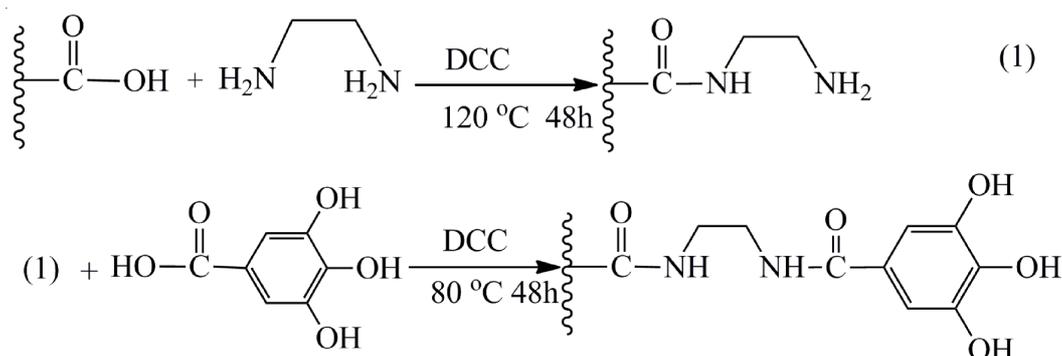


Fig. 1. Synthesis route of AC-ATB

with double distilled water. AC-ATB (25 mg) was subsequently added and the mixture was shaken vigorously for 0.5 h. After extraction, the concentrations of the target metal ions in solution were directly determined by ICP-OES.

Column procedure: The both ends of a home-made glass column (50 mm × 2.5 mm i.d.) were plugged with a fraction of glass wool and then 15 mg AC-ATB was packed in the column. After cleaning by passing through 10 % HNO₃ solution and double distilled water once more, the column was accommodated to the required pH value with 0.1 mol L⁻¹ HCl. Sample solutions were flowed through the column at a flow rate of 1 mL min⁻¹. Afterwards, the metal ions were stripped off from the column with eluent containing 4 mL of 6 % CS(NH₂)₂-3 mol L⁻¹ HCl. The target metal ions in the eluent were determined by ICP-OES.

RESULTS AND DISCUSSION

Characterization of AC-ATB: The FT-IR spectra of AC-COOH, AC-EDA and AC-ATB are shown in Fig. 2. According to the spectrum of AC-COOH, a characteristic peak at 1703.21 cm⁻¹ is assigned to the C=O stretching vibration of the carboxylic acid group. The 4 peaks of varying intensity between 1650 and 1400 cm⁻¹ reflect the presence of benzene ring for its skeleton vibration, the peak at 3327.10 cm⁻¹ could be assigned to phenolic hydroxyl group and the out-of-plane bending vibrations of O-H were at 759.80 and 643.94 cm⁻¹. Furthermore, the new peaks at 1437.61 and 1624.59 cm⁻¹ are caused by the stretching vibration of C-N and N-H in AC-ATB, which indicate that AC-ATB is successfully synthesized^{22,23}.

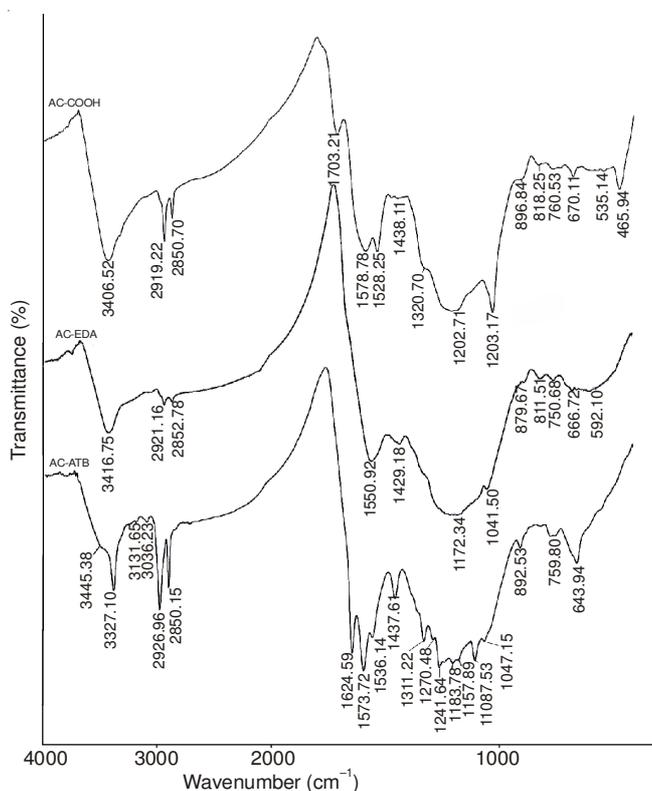


Fig. 2. FT-IR spectra of AC-COOH, AC-EDA and AC-ATB

Compared with 61.13 % of carbon, 2.69 % of nitrogen and 2.97 % of hydrogen in AC-COOH, the elemental analysis data of AC-ATB are 68.16 % of carbon, 9.33 % of nitrogen and 5.39 % of hydrogen which possesses higher carbon and nitrogen content existed in AC-ATB. The result confirms that *N*-aminopropyl-(3,4,5-trihydroxy) benzamide is successfully used to modify activated carbon which is consistent with the FT-IR analysis results mentioned above.

SEM analysis: SEM micrographs of the AC and AC-ATB are shown in Fig. 3. The result (Fig. 3a) shows that the activated carbon turned out to be a layered structure. Compared to the AC, the AC-ATB was found of small spherical particles with dendritic connections (Fig. 3b), which is attributed that AC-ATB with three-dimensional structure and tiny aperture on its surface possesses advantages in terms of adsorption capacity and selectivity in comparison with unmodified activated carbon.

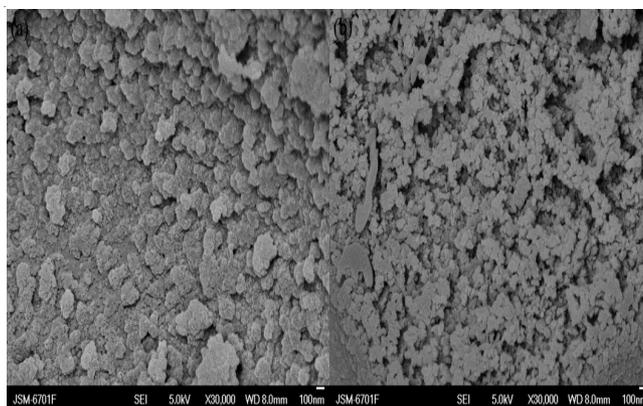


Fig. 3. Scanning electron microscopy (SEM) micrographs of the sample of AC (a) and AC-ATB (b)

Effect of analytical conditions

Effect of pH: The selective adsorption of carbon materials for metal ions in aqueous solution depends on the chemical modification on activated carbon surface and experimental conditions. The proton exchange on carbon surface plays an extraordinary role in the formation of metal complexes²⁴, therefore, as a momentous factor for quantitative adsorption onto adsorbent, the pH value of the solution is explored.

Following the batch procedure, the adsorption of Au(III), Pd(II), Pt(IV), Rh(III) and Ru(III) ions on AC-ATB was studied at different pH values (from 0 to 4). The results showed that the highest metal adsorption values (Fig. 4) were found for simultaneous preconcentration of Au(III), Pd(II) and Pt(IV) ions by AC-ATB in range pH of 1-3. Meanwhile, Ru(III) and Rh(III) could be adsorbed by AC-ATB to 21-68% and around 15% independently under the same condition of acidity. Tracing it to its cause that intense competition caused by excessive chloride limits, the recoveries of metal ions chelated in higher concentrations of hydrochloric acid and many metals ions could hydrolyze and precipitate in the relatively high²⁵ pH. Thus, pH 2 was selected as the enrichment acidity for the following study.

Effect of AC-ATB mass: In order to quantitatively obtain the target metal ion retention, appropriate adsorbent quality should be adopted. Different amounts of AC-ATB (range from

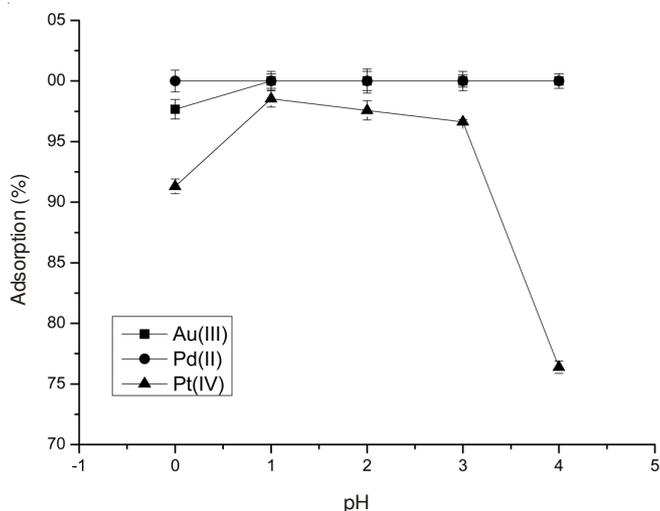


Fig. 4. Effect of pH on analyte adsorption; Au(III), Pd(II) and Pt(IV): $1 \mu\text{g mL}^{-1}$; sample volume: 10 mL; AC-ATB amount: 25 mg; shaking time: 0.5 h; temperature: 20°C

10 to 30 mg) were added to several micro-extraction columns. Then 10 mL ($1 \mu\text{g mL}^{-1}$) solutions containing Au(III), Pd(II) and Pt(IV) at pH 2 flowed slowly through these micro-columns, which results were shown in Fig. 5. Quantitative adsorptions for all the three metal ions were not obtained when the quantity of AC-ATB was less than 15 mg. To conserve the amount of adsorbent and enhance the flow rate, the AC-ATB mass was selected 15 mg for further study.

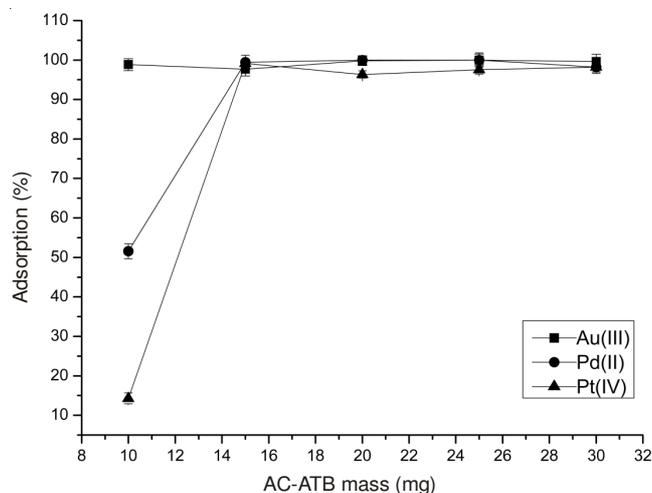


Fig. 5. Effect of mass on analyte adsorption; Au(III), Pd(II) and Pt(IV): $1 \mu\text{g mL}^{-1}$; sample volume: 10 mL; pH 2; temperature: 20°C

Effect of flow rate: The flow rate of the sample solution is a very significant parameter for the retention of ions on sorbent. Therefore 15 mg of AC-ATB was placed in the micro-column and 10 mL of sample solution containing Au(III), Pd(II) and Pt(IV) ions passed through it. The flow rates were adjusted in range of $0.2\text{--}1.4 \text{ mL min}^{-1}$ with a peristaltic pump. As shown in Fig. 6, the adsorptions of the studied ions decreased with increasing of the flow rate. When the flow rate was less than or equal to 1 mL min^{-1} , the quantitative adsorption of target metal ions could be achieved. Hence, to obtain quantitative adsorption of analyte and avoid the extension of analysis time²⁶, a flow rate of 1 mL min was employed in this work.

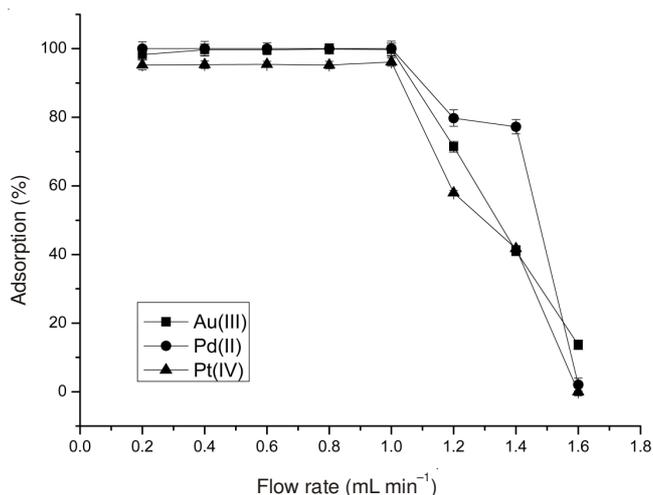


Fig. 6. Effect of flow rate on analyte adsorption; Au(III), Pd(II) and Pt(IV): $1 \mu\text{g mL}^{-1}$; sample volume: 10 mL; AC-ATB amount: 15 mg; pH 2; temperature: 20°C

Conditions for elution: It is well-known that the elution condition plays an important role in the adsorption of target ions. It was reported that the noble metal ions adsorbed were not easy to get rid completely after the saturated adsorption since the noble metal ions were discovered to be decreased to their metallic states in the adsorption procedures¹. The target ions enriched on AC-ATB were eluted with different concentrations of dilute HCl, HNO_3 , $\text{CS}(\text{NH}_2)_2$ and $\text{HCl-CS}(\text{NH}_2)_2$ solutions, separately. However, it was found that Au(III), Pd(II) and Pt(IV) could not be eluted by individual HCl, HNO_3 or $\text{CS}(\text{NH}_2)_2$. In comparison, the $\text{HCl-CS}(\text{NH}_2)_2$ solution in different proportions was serviceable in order to achieve satisfactory desorption of the analytes from the column. By fixing the concentration of HCl at 0.2 mol L^{-1} , the effect of thiourea concentration for desorption of the target ions was indagated with different concentrations of thiourea from 1 to 8 % (m/v). The results suggested that the recoveries of Au(III), Pd(II) and Pt(IV) increased with rising the concentration of thiourea, which could be attributed to that thiourea was of stronger chelating properties to these three noble ions than functional group on AC-ATB. Take account of certain influence on the ICP-OES determination in higher concentrations of thiourea, 6 % (m/v) of thiourea was chosen in this work. Various concentrations HCl-6 % thiourea were used for the desorption of Au(III), Pd(II) and Pt(IV) ions following the above procedure. It was concluded that quantitative elution could be achieved with 3 mol L^{-1} HCl-6 % thiourea.

For the purpose of acquiring the minimum volume of eluent quantificationally, a series of volumes from 1 to 10 mL were experimented when 3 mol L^{-1} HCl-6 % thiourea was selected. It was finally found that 4 mL of 3 mol L^{-1} HCl-6 % (m/v) thiourea was an efficient eluent.

Regeneration studies: For the regeneration of adsorbent in column experiments, several adsorption and desorption operations were repeatedly carried out. After repeated eleven times through the column, the recoveries of Au(III), Pd(II) and Pt(IV) were less than 95 %. The adsorbent displayed better long-term stability and reusability towards Au(III), Pd(II) and Pt(IV) ions.

Maximum sample volume and enrichment factor: In order to explore the possibility of enrichment in low concentration of the target ions from large volumes, the maximum applicable volume of sample that can be passed through the column loaded with AC-ATB must be determined. 50-500 mL of sample solutions containing 5 µg Au(III), Pd(II) and Pt(IV) ions passed through the micro-column under the optimum conditions. Quantitative recoveries (> 95 %) of these three ions were obtained in the sample volume of 400 mL and the further increase of the sample volume caused evident decrease of the recoveries. The enrichment factor for simultaneous preconcentration and extraction is calculated by the ratio of the maximum sample volume for analyte (400 mL) and the lowest final eluent volume (4 mL). Therefore, the enrichment factor was 100 in this work.

Adsorption capacities: The adsorption capacity is also an important factor because it reflects how much adsorbent is required to quantitatively enrich the analytes from the solution. The adsorption capacity research was introduced from the document recommended by Maquieira *et al.*²⁷. 10 mL of various concentrations (10-500 µg mL⁻¹) containing Au(III), Pd(II) and Pt(IV) ions solutions were adjusted to the appropriate pH and followed the column analysis program with 15 mg of AC-ATB. The amount of Au(III), Pd(II) and Pt(IV) adsorbed on per unit mass of sorbent increased with concentration of metal ions heightened till the steady values (adsorption capacity values) were obtained. The saturated adsorption amount of AC-ATB for Au(III), Pd(II) and Pt(IV) ions was found to be 195.7, 95.1 and 99.3 mg g⁻¹, respectively. The results suggested that AC-ATB possesses a higher adsorption capacity for Au(III), Pd(II) and Pt(IV) ions.

Effect of potentially interfering ions: It is well known that, in most cases, the metal ions do not exist individually. Therefore, it is necessary to investigate the adsorptions of target ions accompanied by other coexisting ions. Different interfering ions were added to quantitative analyte ions solutions and then the solutions were enriched and determined according to the column procedure. As shown in Table-1, 50 fold excess of Fe³⁺, Hg²⁺, Zn²⁺, Ni²⁺, Cu²⁺, Pb²⁺, Mn²⁺, Rh³⁺, Ru³⁺, Ir⁴⁺ and 1000 fold excess of K⁺, Na⁺, Mg²⁺, H₂PO₄⁻ ions did not influence

TABLE-1
EFFECT OF INTERFERING IONS ON ADSORPTION
OF 1.0 µg mL⁻¹ Au(III), Pd(II) AND Pt(IV)

Coexisting ion	Concentration (µg mL ⁻¹)	Adsorption (%)		
		Au(III)	Pd(II)	Pt(IV)
Fe ³⁺	50	99.2	96.7	95.4
Hg ²⁺	50	99.0	95.1	96.0
Zn ²⁺	50	98.6	100	97.1
Ni ²⁺	50	99.3	100	97.7
Cu ²⁺	50	99.9	100	95.3
Pb ²⁺	50	99.6	100	98.5
Mn ²⁺	50	99.7	100	96.9
Rh ³⁺	50	100	95.1	97.6
Ru ⁴⁺	50	99.2	100	96.1
Ir ⁴⁺	50	96.9	100	96.3
K ⁺	1000	98.7	97.5	96.5
Na ⁺	1000	98.8	98.1	96.4
Mg ²⁺	1000	99.0	100	96.5
H ₂ PO ₄ ⁻	1000	100	100	95.1

the determination of study ions. The high adsorptions (> 95 %) of Au(III), Pd(II) and Pt(IV) ions showed that adsorbents obtained could be used for analysis of actual samples in the presence of interfering ions.

Analytical precision and detection limits: Eight portions of mixed standard solutions (1.000 µg mL⁻¹) were enriched and analyzed synchronously following the analytical procedure under the optimum conditions. The relative standard deviations (RSDs) of the method were less than 3 % [Au(III):1.7 %, Pd(II): 2.8 %, Pt(IV): 0.8 %]. According to the detection limit (3σ) defined by IUPAC, it was found to be 7, 11 and 6 ng mL⁻¹ for Au(III), Pd(II) and Pt(IV), respectively, which was calculated based on three times the standard deviation of 11 runs for the blank solution. These results demonstrated that the method possessed good precision and low detection limit for the analysis of trace Au(III), Pd(II) and Pt(IV) ions in solution samples.

Application of method: For checking the accuracy of the procedure given above, the proposed method was applied to the determinations of trace Au(III), Pd(II) and Pt(IV) ions in the certified reference material (GBW 07808 and GBW 07293). Table-2 showed that the analytical results for the standard materials were in good agreement with the certified values.

The developed preconcentration procedure was also applied for alloy sample using the standard addition method for calibration. Table-3 showed that the recoveries for Au(III), Pd(II) and Pt(IV) ions were in the range of 94.8-103.6 %. The results indicated that the proposed method for trace noble metal ions in actual sample was satisfactory.

TABLE-2
ANALYTICAL RESULTS OF Au(III) IN GBW07808
AND Pd(II) AND Pt(IV) IN GBW07293
GEOLOGICAL REFERENCE MATERIAL

Sample	Found ^a (µg mL ⁻¹)	Certified value (µg mL ⁻¹)
GBW07808 Au(III)	3.18 ± 0.12	3.20 ± 0.10
GBW07293 Pd(II)	0.564 ± 0.074	0.568 ± 0.051
Pt(IV)	0.422 ± 0.058	0.440 ± 0.037

^aThe value following "±" is the standard deviation (n = 5)

TABLE-3
RESULTS FOR DETERMINATION OF Au(III),
Pd(II) AND Pt(IV) IN ACTUAL SAMPLE

Sample	Added (µg mL ⁻¹)	Found ^a (µg mL ⁻¹)	Recovery (%)
Alloy sample			
Au(III)	0	1.440 ± 0.011	-
	0.5	1.936 ± 0.055	99.8
	1.0	2.452 ± 0.035	101.5
Pd(II)	0	0.037 ± 0.019	-
	0.5	0.509 ± 0.017	94.8
	1.0	1.006 ± 0.041	97.0
Pt(IV)	0	n.f. ^b	-
	0.5	0.511 ± 0.026	102.2
	1.0	1.036 ± 0.023	103.6

^aThe value following "±" is the standard deviation (n = 5)

^bn.f., not be found

Comparison with other methods: The adsorption capacities of AC-ATB were compared with other reported methods on preconcentration of Au(III), Pd(II) and Pt(IV).

The data were list in Table-4. As seen from the data, the proposed method showed evident higher adsorption capacity compared to other reported methods.

Conclusion

In the present work, an effective new-typed sorbent (AC-ATB) which was characterized by FT-IR spectra, elemental analysis and SEM analysis, has been successfully synthesized and applied to preconcentration of trace Au(III), Pd(II) and Pt(IV) ions as a solid phase extractant prior to their determination by ICP-OES. The sorbent displayed high adsorption capacity, excellent selectivity and good accessibility for the noble metal ions in aqueous solution. In addition, most of the common co-existing ions did not interfere with the determination of target ions under the optimum conditions. The application of the credible method to the analysis of trace Au(III), Pd(II) and Pt(IV) ions in actual sample was performed with satisfactory results.

TABLE-4
COMPARISON OF ADSORPTION CAPACITIES

Adsorbent	Target ions	Adsorption capacity (mg/g)	Ref.
Melamine-formaldehyde-thiourea (MFT) chelating resin	Pd(II)	15.29	[28]
Tris(hydroxymethyl)aminomethane modified activated carbon	Au(III)	33.57	[29]
Fe ₃ O ₄ nanoparticles	Pd(II) Pt(IV)	10.961 13.265	[30]
N-Aminopropyl-(3,4,5-trihydroxy) benzamide modified activated carbon	Au(III) Pd(II) Pt(IV)	195.7 95.1 99.3	This work

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