Preparation and characterization of magnetic nanoparticles for the on-line determination of gold, palladium, and platinum in mine samples based on flow injection micro-column preconcentration coupled with graphite furnace atomic absorption spectrometry

Juanjuan Ye [a], Shuxia Liu [a], Miaomiao Tian [a], Wanjun Li [a], Bin Hu [b], Weihong Zhou [a], Qiong Jia [a,*]

[a] College of Chemistry, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

ABSTRACT

A simple and highly selective procedure for on-line determination of trace levels of Au, Pd, and Pt in mine samples has been developed using flow injection-column adsorption preconcentration coupled with graphite furnace atomic absorption spectrophotometry (FI-column-GFAAS). The precious metals were adsorbed on the as-synthesized magnetic nanoparticles functionalized with 4′-aminobenzo-15-crown-5-ether packed into a micro-column and then eluted with 2% thiourea$+0.1$ mol L^{-1} HCl solution prior to the determination by GFAAS. The properties of the magnetic adsorbents were investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM). Various experimental parameters affecting the preconcentration of Au, Pd, and Pt were investigated and optimized. Under the optimal experimental conditions, the detection limits of the developed technique were 0.16 ng mL^{-1} for Au, 0.28 ng mL^{-1} for Pd, and 1.01 ng mL^{-1} for Pt, with enrichment factors of 24.3, 13.9, and 17.8, respectively. Precisions, evaluated as repeatability of results, were 1.1%, 3.9%, and 4.4% respectively for Au, Pd, and Pt. The developed method was validated by the analysis of Au, Pd, and Pt in certified reference materials and mine samples with satisfactory results.

1. Introduction

Direct determinations of trace or ultra-trace levels of metals in geological, metallurgical, and environmental samples are difficult because of their extremely low concentrations together with very complicated sample matrices [1,2]. Thus, a separation and preconcentration procedure is required even with the high sensitivity and selectivity of modern analytical techniques, such as graphite furnace atomic absorption spectrometry (GFAAS) [3,4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5–7], inductively coupled plasma mass spectrometry (ICP-MS) [8–10], adsorptive stripping voltammetry (ASV) [11] or neutron activation analysis (INAA) [12]. Although GFAAS shows similar shortcomings, it is available in most laboratories and has a chance to be in common use over traditional atomic spectrometries. In order to achieve sensitive and reliable results, separation and preconcentration of analytes from the matrix is often necessary prior to GFAAS determinations.

Precious metals have a wide range of potential applications including biological activity, catalysis, jewelry, chemical industry, and surface technology because of their specific physical and chemical properties [13–16]. Due to their low abundance in the earth and their high economic values, several classical separation and preconcentration methods, such as coprecipitation [17], liquid–liquid extraction [4,18], membrane filtration [19], ion-exchange [8], and adsorption [13,20–26] were adopted. Although liquid–liquid extraction can be used to selectively remove precious metals from solutions, it is a time-consuming procedure and requires large quantities of organic solvents. Adsorption seems to be a more suitable method for the separation and preconcentration of precious metals due to simply operating, no or little use of organic solvents, and high efficiency. There are various adsorbents including activated carbon [20,21], biosorbent [15,22], and ion exchange resin [24]. Recently, more and more attention has been gained in the field of sample extraction by magnetic nanomaterials [27–29] due to their unique magnetic response, large surface area, and chemically modifiable surface [30,31]. When organic extractants are modified on the magnetic nanomaterials, the obtained extractant-coated magnetic adsorbents can be packed, dynamically positioned, and repacked in micro-columns by using an external magnetic field placed outside of the extraction container. The whole operation process does not need additional centrifugation or filtration of the sample, which makes sampling and collection easier and faster [32]. To reduce the

* Corresponding author. Tel.: +86 431 85095621.
  E-mail address: jiaqiong@jlu.edu.cn (Q. Jia).

separation time and eliminate the interferences, the extraction and back-extraction steps can be conducted simultaneously if a flow injection technique (FI-column) is used with a micro-column packed with the magnetic adsorbent [27].

Macrocyclic compounds, due to their selective receptor properties and ease of structural modification, have been employed as complexing agents to form stable and selective complexes with alkali, alkaline earth metals, and ammonium cations [33,34]. The high selectivity of macrocycles can be utilized in separation chemistry, such as ion chromatography [33], ion selective electrodes [35], and solvent extraction [36]. 4′-Aminobenzo-15-crown-5-ether (AB15C5), as a benzo condensed crown compound, has the similar chemical properties as solvent extraction reagent, which can prompt crown ether to effectively adsorb analytes through electrostatic and conformational effects, and subsequently coordinate the pairing ion [37]. The combination of magnetic particle and crown ether has potential as a new strategy for the extraction of metal ions and ion pair species, which can incorporate the advantages of magnetic materials and benzo condensed crown compounds. However, to our knowledge, there are no reports about applications of magnetic AB15C5 nanoparticles as sorbents.

In the present work, the crown ether-coated magnetic nanoparticles (hereafter abbreviated as CEMNs) were prepared and used as the adsorption materials for FI-column separation and preconcentration before GFAAS determinations of Au, Pd, and Pt. The synthesized CEMNs possessed high extraction efficiency owing to the nanosize and the abundant functional groups. In order to achieve the best analytical performance, several experimental parameters, such as NaCl concentration, sample pH value, sample loading time, sample flow rate, eluent concentration, and eluent flow rate were optimized. Meanwhile, the accuracy and selectivity of the proposed method were demonstrated by the determination of Au, Pd, and Pt in certified reference mine materials and real geological samples under the optimized conditions.

2. Experimental

2.1. Reagents and materials

The intermediate Au, Pd, and Pt working standard solutions (10 mg L^{-1}) were prepared by appropriate dilution of the stock solutions, 1000 mg L^{-1} for Au (III), Pd (II), and Pt (IV), from Beijing NCS Analytical Instruments Co. Ltd. (Beijing, China, http://www.ncscrm.com). The stock solutions were stored at 4 °C. A series of working standard solutions of the above mentioned elements were daily prepared by dilution of the appropriate amount of stock solutions in 0.1 mol L^{-1} HCl. (3-Aminopropyl) triethoxysilane (APTES, 99%) and sodium cyanoborohydride (NaBH$_3$CN) were purchased from Aladdin Reagent Co. Ltd., China. Certified reference materials, GAu-11b, GBW07289, GBW07291, and GBW07292, were obtained from the National Research Center for Standard Materials (Beijing, China). The geological samples were collected from Heilongjiang province (Heilongjiang, China). All used reagents were of the highest available purity or at least analytical reagent grade. Deionized purified water (DDW) was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

2.2. Apparatus

The experiments were performed using a Shimadzu AA-6300C atomic absorption spectrophotometer equipped with a graphite furnace atomizer GFA-EX7i and an auto-sampler ASC-6100 (Shimadzu, Japan). The hollow cathode lamps and pyrolytic-coated graphite tubes (Shimadzu part no. 206-50588) were used. Deuterium background correction was employed to correct non-specific absorbances. The sample injection volume was 20 μL in all experiments, and output signals were collected and processed in continuous peak height mode. The operating instrumental parameters for all studied elements are listed in Table 1. A model IFIS-D flow injection system (Remex Analyse Instrument Co. Ltd., Xi'an, China) was employed for the separation and preconcentration of precious metals, with the FI manifold shown in Fig. 1. The IFIS-D consisted of two peristaltic pumps, a standard rotary injection valve (8-channel, 16-way rotary injection valve, multifunctional injector), and PTFE tubes (0.8 mm i.d.), with which the sample and reagents were delivered to minimize the dead volume as short as possible. A glassy micro-column (50 mm × 3 mm i.d., Beion Medical Technology Co. Ltd., Shanghai, China) was used for packing the CEMNs. A PB-10 digital pH meter (Sartorius Scientific Instruments Co. Ltd., Beijing, China) was employed for pH measurements.

JSM 6700-F (JEOL Company, Japan) was used to characterize surface morphology of nanocomposites. The structure analysis of the magnetic nanoparticle was carried out using an X-ray Diffractometer (R-AXIS RAPID-F, Rigaku Corporation, Japan) with a detector operating under a voltage of 40.0 kV and a current of 30.0 mA using Cu Kα radiation, and the recorded range of 2θ was 20–80°. The magnetic

Table 1
GFAAS operating parameters.

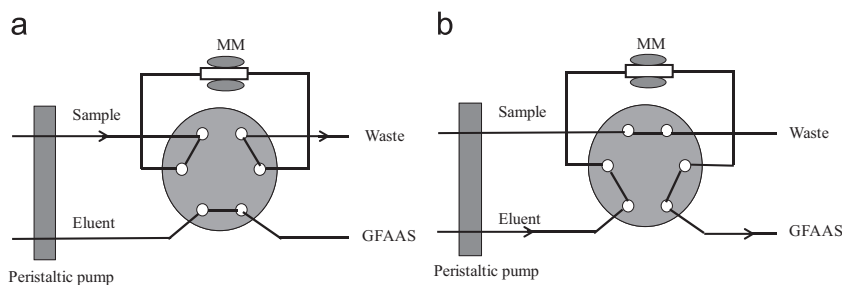|	Wavelength (nm)	Slit width (nm)	Current (mA)	Temperature (°C)				Time (s)			
				Dry	Pyrolysis	Atomizaition	Cleaning	Dry	Pyrolysis	Atomizaition	Cleaning
Au	242.8	0.7	10	150–250	700–700–700	2100	2500	10–10	10–10–3	4	2
Pd	247.6	0.7	10	150–250	1000–1000–1000	2700	2800	20–30	10–10–3	2	2
Pt	265.9	0.7	14	120–250	1200–1200–1200	2600	2650	20–10	10–10–3	3	2

Fig. 1. Diagram of the flow injection procedure. MM, magnetic micro-column and magnet. (a) Load position, (b) Injection position.