Ferrofluid-based dispersive solid phase extraction of palladium

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ABSTRACT

A new mode of dispersive solid phase extraction based on ferrofluid has been developed. In this method, an appropriate amount of ferrofluid is injected rapidly into the aqueous sample by a syringe. Since the sorbent is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds. The ferrofluid can be attracted by a magnet and no centrifugation step is needed for phase separation. Palladium was used as a model compound in the development and evaluation of the extraction procedure in combination with flame atomic absorption spectrometry. The experimental parameters (pH, DDTC concentration, type and concentration of eluent, the amount of adsorbent, extraction time, and the effect of interfering ions) were investigated in detail. Under the optimized conditions, the calibration graph was linear over the range of 1–$100\,\mu g\,L^{-1}$ and relative standard deviation of 3.3% at $0.1\,\mu g\,mL^{-1}$ was obtained ($n=7$). The limit of detection and enrichment factor (EF) was obtained to be $0.35\,\mu g\,L^{-1}$ and 267, respectively. The maximum adsorption capacity of the adsorbent at optimum conditions was found to be $24.6\,mg\,g^{-1}$ for Pd(II). The method was validated using certified reference material, and has been applied for the determination of trace Pd(II) in actual samples with satisfactory results.

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1. Introduction

The importance of the palladium metal has grown in recent years due to characteristics such as the resistance to corrosion and oxidation, high melting points, electrical conductivity, and extraordinary catalytic activity [1]. Palladium and its alloys have an extensive range of applications in the automobile, electronics, metallurgy, catalytic converters, dental and medical prostheses, and jewelry manufacture. Palladium compounds have been regarded as highly toxic and carcinogenic to humans, and easily transported to biological material through plant roots, and ultimately intensified along the food chain. The excessive exposure to palladium causes adverse health effects such as primary skin problems, eye irritations, and substantial degradation of DNA and cell mitochondria. Hence, the separation and determination of palladium is of special interest in environmental analysis. However, the direct determination of these metal ions is often difficult because of low concentration of palladium in industrial and environmental samples and together with complexity of the matrix in real samples. Therefore, preliminary preconcentration of the analyte and matrix separation prior to analysis is often necessary.

Several analytical methods have been employed for separation and preconcentration of Pd(II) prior to its detection, such as coprecipitation, solid phase extraction (SPE), liquid–liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE) and dispersive liquid–liquid microextraction (DLLME) [2–6].

SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility to choose the adsorbent and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices [1,7]. However, because of the limited interface between the sorbent and the aqueous sample, considerable time is needed for the analyte to be extracted onto the sorbent [8]. Thus, a clear trend in analytical chemistry is miniaturization of extraction time. In the last years, the dispersive liquid–liquid microextraction technique has been developed. In this method, an appropriate mixture of the extraction and disperser solvents is injected into the aqueous sample by a syringe to form an emulsified solution. Since the extractant is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds. Despite the many benefits of this method, the choice of the extraction solvent is its main drawbacks [8]. The different modes of DLLME demonstrate that the convenient retrieval of organic solvents after extraction is of crucial importance in such techniques. It is critical, that the extraction solvent be of higher density than that of water, in order to form a stable cloudy solution capable of being separated by centrifuging. However, solvents with their densities higher than that of water are not often compatible with inductively coupled plasma-optical emission spectrometry (ICP-OES) and reverse phase HPLC. So, several

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recent works have reported the use of low-density organic solvents in DLLME. But, most of these procedures require additional processing steps, apart from the mandatory centrifugation, including refrigeration to freeze the organic solvent, manually retrieving it to let it thaw, and use of additional materials such as surfactants [9].

These problems can be avoided by the new technique of dispersive-solid phase extraction (D-SPE) based on a ferrofluid. Ferrofluids are suspensions of single-domain magnetic nanoparticles suspended in various carriers such as water, ester and hydrocarbons. Magnetic suspension characteristically has both magnetic and fluid properties [10–12]. The particle volume fraction of the magnetic material in ferrofluid is typically only a few percent [13,14]. Since the concentration of the magnetic particles is low, 3–10%, many properties of the ferrofluid, such as density, vapor pressure, pour point and chemical properties of the liquid are similar to those of the base fluid. Two types of ferrofluids are available: ionic ferrofluid and surface ferrofluid depending on the method used to prevent the particles from aggregating by Vander Waals forces or magnetostatic interactions [15]. Steric repulsion prevents agglomeration of particles in surface ferrofluid while charged repulsion accounts for the stability in ionic ferrofluid. High stability of a ferrofluid is achieved through a combination of thermal motion as well as steric and electrostatic repulsive interactions [16]. Remote control of the fluid flow by an externally applied magnetic field leads to attractive applications in dynamic loudspeakers, computer hard discs, dynamic sealing, electronic packing, mechanical engineering in high-vacuum equipment, laser systems in audio devices, electromagnetic shielding, high density digital storage, and biomedicine and magnetic cell separation such as enzyme and protein immobilization, genes, radiopharmaceuticals, magnetic resonance imaging MRI and diagnostics [17].

In this method, an appropriate amount of ferrofluid is injected rapidly into the aqueous sample by a syringe. The large contact surface between the sample and the sorbent speeds up the mass transference processes. Since the sorbent is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds.

In the present report, for the first time, a new method of dispersive-solid phase extraction (D-SPE) based on a ferrofluid is proposed. The hydrophobic analytes are enriched in the extraction sorbent which is dispersed into the bulk aqueous solution. This technique is easily carried out.

To the best of our knowledge, there is no report on the use of D-SPE for the separation and preconcentration of inorganic or organic species. The present study has developed a quick method for the extraction of Pd(II) by D-SPE and its determination by FAAS. This method is simple, rapid and efficient for the extraction and preconcentration of Pd(II) from various samples. Furthermore, in comparison with solid phase extraction, it is much faster, since the extractant (sorbent) is highly dispersed in the aqueous phase.

2. Experimental

2.1. Apparatus

A Varian model AA-400 atomic absorption spectrometer (http://www.varianinc.com), equipped with an air–acetylene burner and with palladium hollow cathode lamp was used for the determination of palladium. The lamp was operated at 5 mA, using the wavelength at 244.8 nm and slit of 0.2 nm, and the flow rates of air and acetylene were set as recommended by the manufacturer. Background correction has been used with a deuterium lamp. All measurements were carried out in peak height mode. A pH-meter Model 692 from Metrohm (http://www.metrohm-ag.com, Herisau, Switzerland) equipped with a glass combination electrode was used for the pH measurements. In addition, for magnetic separations a strong neodymium–iron–boron ($Nd_2Fe_{12}B$) magnet (1.31 T) was used. A Field emission scanning electron microscope (FESEM), model S-4160 (www.hitachi.com/procurement/network/japan) was used for preparation of SEM images.

2.2. Reagents

All chemicals used were of analytical-reagent grade and all aqueous solutions were prepared using ultrapure water. 1-Octanol, sodium diethyldithiocarbamate trihydrate (DDTC), acetylacetone, acetic acid, tetraethyl orthosilicate (TEOS), and all used salts were purchased from Merck (Darmstadt, Germany). Standard stock solutions of Pd(II) were prepared by dissolving spectral pure grade chemical $PdCl_2$ (1000 µg mL^{-1} in 5% HNO_3; Merck, Darmstadt, Germany) in double distilled water with the addition of 5 mL of 12 mol L^{-1} nitric acid and further diluted daily prior to use. A solution of 10^{-3} mol L^{-1} DDTC was prepared by dissolving appropriate amount of this reagent in pure ethanol. Nano-Fe_3O_4 was purchased from Sigma-Aldrich (http://www.sigmaaldrich.com, Fe_3O_4 spheres powder, < 50 nm, purity > 98%). A buffer solution (pH=6.0, 1 mol L^{-1}) was prepared by mixing 50 mL potassium dihydrogen phosphate (1 mol L^{-1}) and 5.7 mL of sodium hydroxide (1 mol L^{-1}). High purity HNO_3 (65%, r ultrapure, Merck, Darmstadt, Germany), and HCl were used for digesting of dust sample throughout this work. The pipettes and vessels were cleaned before use by soaking in 10% nitric acid solution for at least 24 h and then rinsed thoroughly with ultrapure water.

2.3. Preparation of silica-coated magnetite nanoparticles

Fe_3O_4/SiO_2 NPs were synthesized according to the previously reported methods by some modification [18]. Briefly, Fe_3O_4 nanoparticles (2.0 g) were suspended in ethanol (200 mL) under sonication for 1 h. Concentrated ammonia (40 mL), deionized water (35 mL) and TEOS (1 mL) were added in sequence to the suspension. The mixture was sonicated for 1 h followed by vortex mixing for another 8 h. The silica-coated nanoparticles (SCMNPs) were collected by magnetic separation and were thoroughly washed with deionized water three times and then dried, yielding a fine powder. Fig. 1 shows the SEM image of the modified nanoparticles.

2.4. Sample preparation

The reference material GBW-07289 (soil) was employed for testing the accuracy of developed method.

Samples of road dust were collected from three different roadsides with dense traffic in Tehran. An amount of 1.0 g of homogenized dust sample was weighed accurately and digested with 3:1 HCl/HNO_3 in a 200 mL beaker by refluxing the mixture for 5 h. The solution of each sample was centrifuged and filtered. The filtered solution was diluted with distilled water up to 100 mL and pH of solution was adjusted to 6.0. Then 50 mL of this solution was poured into a Falcon tube. The obtained solution was analyzed following the experimental procedure.