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Trace determination of palladium in road dust samples by ET-AAS after microwave assisted digestion and preconcentration on magnetite nanoparticles

Y.Ghorbani*[1], H.Farahani[2], A.Rahimi[3], S.M.Shoja[1]

[1]Analytical Chemistry Group, Research Institute of Petroleum Industry (RIPI), Tehran, (IRAN)
[2]Environmental Protection Department, Research Institute of
Petroleum Industry (RIPI), Tehran, (IRAN)
[3]Electrochemistry and Inhibitors Group, Environmental Protection Department,
Research Institute of Petroleum Industry (RIPI), Tehran, (IRAN)
E-mail : Ghorbaniy@ripi.ir

Abstract : A simple and efficient microwave assisted digestion (MAD) combined with alumina-coated magnetite nanoparticles (MNPs) preconcentration method followed by electrothermal atomic adsorption spectrometry (ET-AAS), was developed for trace determination of palladium (II) (Pd^{+2}) in road dust samples. In the proposed approach, Pd^{+2} after chelate formation with 1-(2-pyridilazo)-2-naphthol (PAN), was quantitatively extracted to the surface of Al_2O_3-coated Fe_3O_4 MNPs. Then, elution of the preconcentrated metal from the surface of the Al_2O_3-coated Fe_3O_4 MNPs was performed prior to its determination by ET-AAS. The effects of pH, PAN concentration, SDS and Fe_3O_4 MNPs amounts and interfering ions on the recovery of the analyte were investigated. Under optimized conditions, the calibration curve was linear in the range of 0.5-100 $\mu g\ L^{-1}$ with regression coefficient corresponding to 0.998. The values of the detection limit (based on $3S_b$) and relative standard deviations (RSDs, for 10.0 $\mu g\ L^{-1}$ of the analyte) were 0.045 $\mu g\ L^{-1}$ and below than 3.9% ($n = 10$). The accuracy of the method was tested by the recovery experiments on spiked real samples, with results ranging from 96 to 105%. Finally, the method was successfully applied for determination of Pd^{+2} in several road dust samples and satisfactory results were obtained.

Keywords : Palladium; Electrothermal atomic adsorption spectrometry; Magnetite nanoparticles; Microwave assisted digestion; Road dust samples.

INTRODUCTION

Recently, palladium (Pd) is attracting a lot of attention in various fields, such as industry, technology and medicine due to its excellent chemical and physical characteristics[1,2]. Its main industrial uses are raw materials for catalysts (e.g. auto catalyst), semiconductors and alloys[3,4]. Studies on Pd concentrations in ancient ice and recent snow samples reflect the increase in mining, smelting and use of the metal in the last decades[5].

An increase of Pd in the environment has been shown in air and dust samples[6-9]. Although the concentration of the metal in different compartments of environment continuously increases, it is still at the level of $\mu g\ Kg^{-1}$ (or $\mu g\ L^{-1}$). Environmental or industrial pollutions by Pd have so far been hardly reported as compared with toxic heavy metals like cadmium, mercury and lead[10]. However, the long-term exposure to Pd may affect the human health and the growth of living beings in the future[11,12]. So, the monitoring of Pd in environmental samples has great importance with respect to estimation of the future risk of the human health and the ecosystem.

Several techniques such as flame atomic absorption spectroscopy (FAAS)[13-15]. Graphite furnace-atomic absorption spectrometry (GF-AAS)[16-19], inductively coupled plasma-atomic emission spectrometry (ICP-AES)[20,21], neutron activation analysis (NAA)[22]. inductively coupled plasma mass spectrometry (ICP-MS)[23,24] and ultraviolet–visible spectrometry (UV-Vis)[25,26] have been used for determination of Pd.

However, numerous interactions between the analyte and the matrix constituents can significantly influence both the limit of detection and the accuracy of the analytical techniques. The direct determination of Pd in environmental samples by the methods is usually difficult, and an initial sample pretreatment is often necessary.

Several methods have been reported for the separation and preconcentration of the metal ions, such as coprecipitation[27], liquid-liquid extraction (LLE)[28,29], solid-phase extraction (SPE)[13,30-33] and cloud point extraction (CPE)[34,35], but the disadvantages such as time-consuming, unsatisfactory enrichment factors, large organic solvents and secondary wastes, limit their applications.

Magnetic Nanoparticles (MNs) are magnetic iron oxides that have a super paramagnetic behavior under certain particle sizes, which can be easily magnetized with an external magnetic field and redispersed immediately, once the magnetic field is removed. MNs have been widely used in various industrial products, for example pigments, recording materials, printing and electro photography, such as copying toner and carrier powders, etc.[36-41], since they have excellent physicochemical properties. In recent years, MNs have been applied to the separation of trace organic compounds and metal ions in various samples[42-47]. A major advantage of using MNs as solid phase extractor is the possibility of the collection of MNs by application of a magnetic field in a batch system. This makes magnetic nanoparticles excellent candidates for combining adsorption properties with ease of phase separation. In addition, high surface area and surface charge density, depending on the pH, are some of the advantages.

The aim of the present study was to investigate the applicability of MAE with MNs followed by ET-AAS method for road dust monitoring of Pd^{+2}. The factors affecting the extraction efficiency were studied in detail and the optimal conditions were established. The method was validated for quantitative purposes, and then applied to real sample analysis.

EXPERIMENTAL

Instrumentation

A PerkinElmer (AAS 5100PC, USA) ET-AAS equipped with Zeeman-effect background correction and an AS-20 auto sampler was used for Pd^{+2} analysis. Absorbance measurements were carried out at 247.6 nm using Pd hollow cathode lamp (from PerkinElmer) operated at 8.0 mA with deuterium background correction (at 12 mA). The instrumental parameters were used according to the manufacturer's recommendations. All measurements were based on peak area. The instrumentation parameters are listed in TABLE 1.

TABLE 1 : Parameters for ET-AAS measurement.

Instrument	Perkin-Elmer 5100
Lamp type, power	HCL, 8.0 mA
Wavelength	247.6 nm
Slit width	0.7 nm
Signal measurement	Peak height
Integration time	5 s
Background correction	Zeeman

TABLE 2 : Operating parameters for the used high pressure vessels.

Parameter	Medium pressure vessel (PTFE-TFM)
Number of vessels	16
Vessel design	PEEK pressure with PTFE-TFM liner screw cap with metal safety and venting screw
Vessel volume	100 mL
Max. fulling	50 mL
Maximum operation pressure	70 bars
Working pressure	18 bar (260 psi)
Maximum operation temperature	190 ^{o}C
Reaction control	Optional reference vessel with p-sensor accessory or P/T sensor accessory, optional IR sensor
Maximum of power	900 W

An ultrasonic bath (QH Kerry, Germany) and a multi-wave microwave sample preparation system (Anton Paar, Multiwave 3000, Austria) equipped with up to 12 tetrafluorometoxil (TFM) vessels was used in sample preparation procedure. The pressure, temperature and microwave energy in Anton Paar system was controlled; Technical data and recommended experimental conditions for the applied TFM liners are given in TABLE 2. The pH of the solutions was measured with a WTW pH meter (Inolab, Germany) which was supplied with a combined pH electrode.

Reagents

All chemicals used were of analytical reagent grade. Ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$), sodium hydroxide, 1-(2-pyridilazo)-2-naphtol (PAN), palladium nitrate, sodium dodecyl sulfate (SDS), nitric acid and hydrochloric acid was all purchased from Merck (Darmstadt, Germany). The working solutions were obtained daily by appropriately diluting the stock solution with pure water. The used reagent water was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Preparation of MNPs

The magnetic adsorbents, alumina-coated magnetite nanoparticles (Fe_3O_4/Al_2O_3 MNPs), were synthesized by alkoxide hydrolysis precipitation method[48]. Ferrous chloride (2.0 g), ferric chloride (5.2 g), and hydrochloric acid (12 M, 0.85 mL) were dissolved in 25 mL water. The mixture was added drop wise into 250 mL NaOH solution (1.5 M), under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction. After the reaction, the obtained Fe_3O_4 MNPs precipitate magnetic field, and rinsed with 200 mL water four times. Then, the product was oven dried at 80 °C. Aluminum isopropoxide (1.0 g) was dissolved in ethanol (60 mL) to form a clear solution. Fe_3O_4 MNPs (0.1 g) were then dispersed in the freshly prepared solution for 5 min with the aid of ultrasonic. A mixture of water and ethanol (1:5, v/v) was added drop wise to the suspension of Fe_3O_4 MNPs with vigorous stirring. The mixture was stirred for half an hour after addition. Subsequently, the suspension was standing for one hour before separating and washing with ethanol. After five cycles of separation/washing/redispersion with ethanol, the powder obtained was oven dried and calcined at 500 °C for three hours.

Preparation of mixed hemimicelles particles

For the preparation of mixed hemimicelles particles firstly, 0.05 g Fe_3O4/Al_2O_3 MNPs and 40 mg SDS and 9.0 mg L^{-1} PAN solutions were added into 250 mL water and the pH was adjusted to 2-2.5 with 3 M HCl solutions and then were shaked mechanically for 15 min to form mixed hemimicelles assemblies. Subsequently, on the SDS-PAN coated Fe_3O_4/Al_2O_3 MNPs were isolated by placing a strong magnet and the supernatant was poured away and there were washed with high purity deionized water.

Sample solution (containing Pd^{+2} in the range of 0.5-100 $\mu g\ L^{-1}$) was prepared and the pH value was adjusted to 4 with 0.1 M HCl and NaOH solutions was added into the SDS-PAN coated Fe_3O_4/Al_2O_3 MNPs and then were shaked mechanically for 15 min. Subsequently, the SDS-PAN coated Fe_3O_4/Al_2O_3 MNPs were isolated by placing a strong magnet and the supernatant was poured away. The preconcentrated target analyte absorbed on SDS-PAN coated Fe_3O_4/Al_2O_3 MNPs was eluted with using 1 mL of 2 M HNO_3. The analytes in the effluent were determined by ET-AAS.

Dust samples

Road dust samples were taken from various locations of Tehran streets and highways (Hemmat highway, Hakim highway, Towhid tunnel and Azadi street), using a small brush and a plastic pan. The samples were dried in an oven at 120 °C for 24 h. sieving of the material was not required. The PTFE vessels of the multiwave system are charged with 0.3 g of dust, 5 mL of HNO_3 (65 wt. %), and 2 mL of H_2O_2 (31 wt. %). Solid particles attached to the wall of the Tetraflourometoxil (TFM) liner should be rinsed when the first vigorous reaction has taken place, the pressure vessels are closed and the first microwave step is performed. When opening the vessels after they have cooled down, nitrous gases escape and in most cases a precipitation of silicate is observed. For the second step, 3 mL of hydrofluoric acid (49 wt. %) is added. The vessels are closed and heated according to step 2 in. After they have cooled down, they are opened again and 5 mL of a saturated H_3BO_3 solution are added for the third reaction step. In this step, no further gaseous reagent products are formed-only masking of fluoride takes place. The digestion solutions are then transferred into 50 mL glass flasks, filled up to volume with the reagent water.

RESULT AND DISCUSSION

A univariate approach was employed to optimize the influential factors in this method. Quantifications were based on the peak height the analyte based on the average of five replicate measurements. In order to study the performance parameters, the extraction recovery were employed.

Effect of pH

The pH plays an important role in the complexation of palladium with PAN and is one of the factors influencing the adsorption behavior of mixed hemimicelles system due to the change of the charge density on the Fe_3O_4/Al_2O_3 MINPs surface. The percent sorption of palladium ion on the sorbent surface as a function of the pH of the sample solution was examined in the range of 1.0-8.0. As can be seen from Figure 1, the percent sorption of Pd (II) depends on the pH of the sample solution. In subsequent studies, the pH was maintained at approximately 4.0.

Effect of PAN concentration

PAN acts as a tridentate ligand and can form very stable complexes with metal ions (as ML or ML_2) through hydroxyl oxygen atom, nitrogen atom of pyridine and one of the azo group nitrogen atoms[49]. PAN

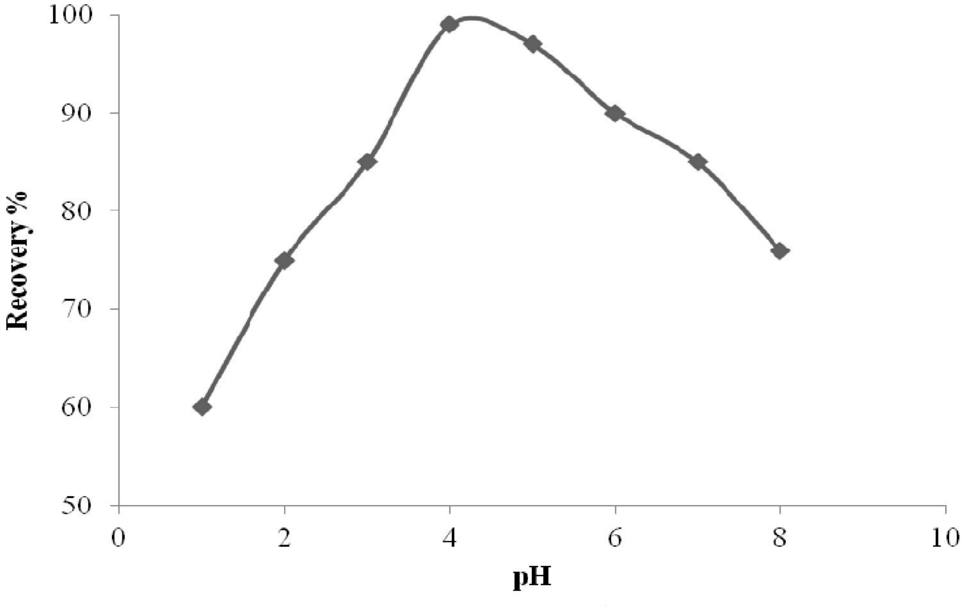

Figure 1 : Effect of pH on the adsorption of Pd, condition: PAN (5.4×10^{-4}M), SDS (54 g), Fe_3O_4/Al_2O_3/NPs (80 g), Pd (10 ng mL^{-1}).

complexes of Pd (II) can be easily interacted with SDS-coated Fe_3O_4 /Al2O3 NPs, which increases extraction efficiency of the analyte. At 10 µg L^{-1} of the metal, the effect of PAN concentration on extraction efficiency was studied by changing the molar ratio of PAN to Pd (II) in the range of 0.9×10^{-4}- 12×10^{-4} M (Figure 2) Results indicated that the signal increases up to a PAN concentration of 5.4×10^{-4} M, reaching the plateau afterwards which is considered as 100% extraction. Hence, PAN concentration of 5.4×10^{-4} M was employed throughout the work.

Effect of the amounts of the surfactant

The adsorption of surfactant on the surface of mineral oxides can be divided into three regions (hemimicelles, mixed hemimicelles and admicelles). From Figure 3 we can see that in the presence of SDS, the Pd was hardly adsorbed on to the surface of PAN-Fe_3O_4/Al_2O_3 NPs. The adsorption amount of Pd increased remarkably with the increasing amount of SDS. Giving the findings, 54 mg was selected as the final addition amount of SDS in the studies.

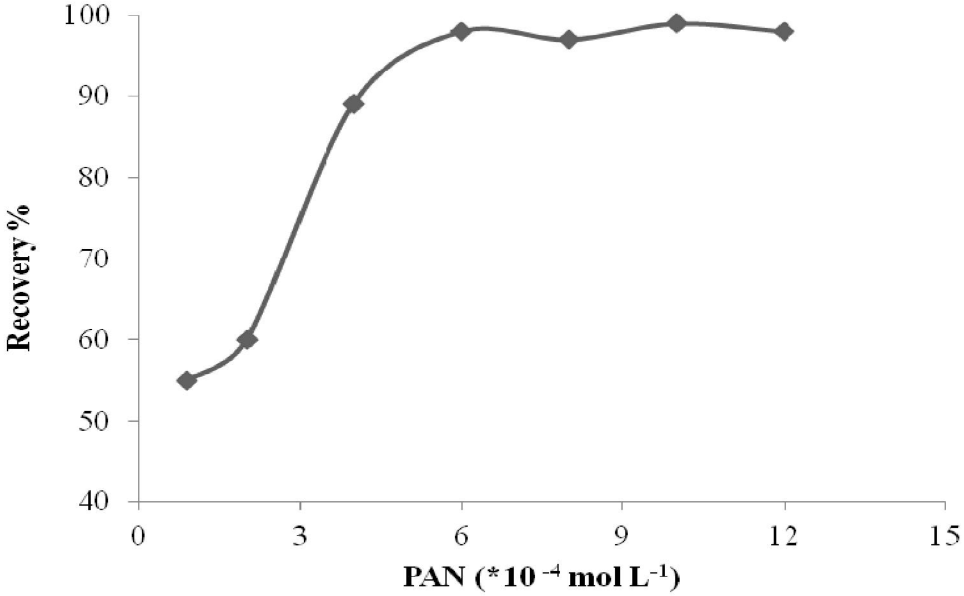

Figure 2 : Effect of the amount PAN on the adsorption of Pd, conditions: SDS (54 mg), Fe_3O_4/Al_2O_3/NPs (80 mgr), Pd (10 ng mL^{-1}).

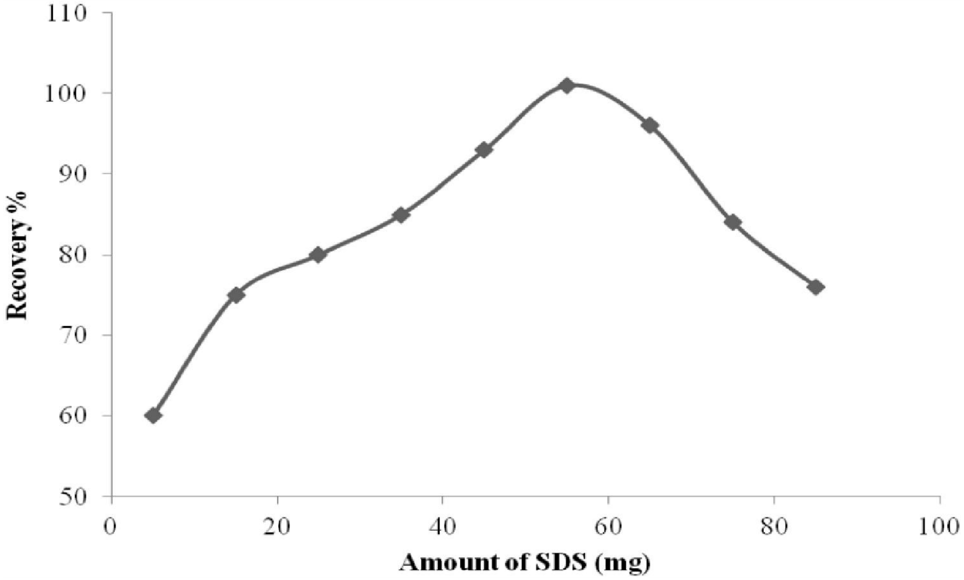

Figure 3 : Effect of amount of SDS added on the adsorption of Pd, conditions: PAN (5.4×10^{-4} M), Fe_3O_4/Al_2O_3/NPs (80 mg), and Pd (10 ng mL^{-1}).

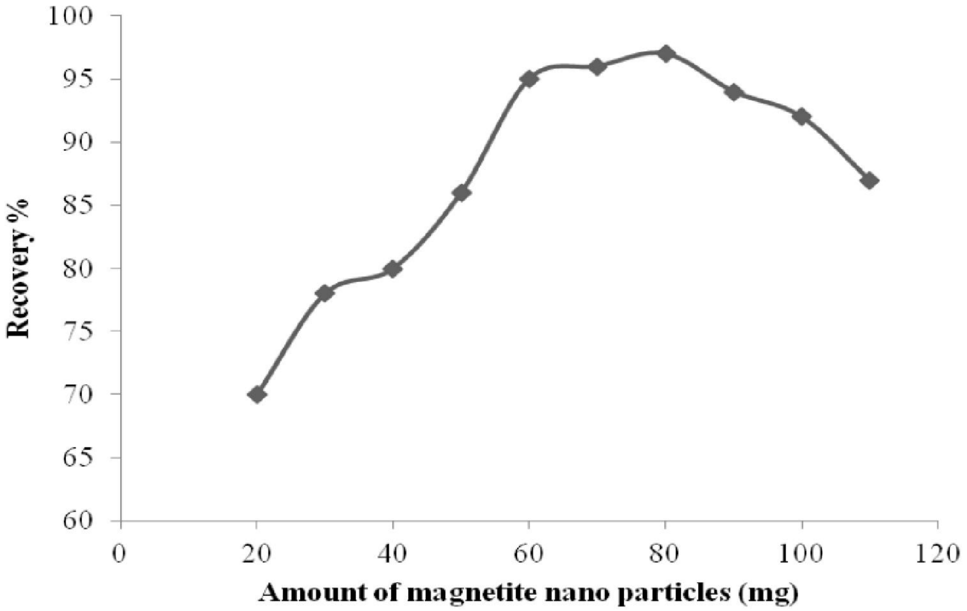

Figure 4 : Amount of adsorbent added on the adsorption of Pd, conditions: PAN (5.4 × 10^{-4} M), SDS (54 g) and Pd (10 ng mL^{-1}).

Effect of the adsorbent amount and extraction time

In comparison with traditional sorbents, MNPs offer a significantly higher surface area to volume ratio. Therefore satisfactory results can be achieved with fewer amounts of NPs. In order to study the effect of adsorbent, 20 -200 mg Fe_3O_4/Al_2O_3/NPs was added to 50 ml sample solution. As shown in Figure 4 the results indicated that quantitative recovery of Pd was obtained with increasing of modified Fe_3O_4/Al_2O_3/NPs amount of 80 mg. So an 80 mg of Fe_3O_4/Al_2O_3/NPs was selected for all subsequent experiments.

The effect of extraction time was examined in the range of 10 min to 3 h with the optimized constant experimental conditions. The obtained results showed that palladium adsorption occurred rapidly in the first 30 min.

Evaluation of the method performance

To evaluate the practical applicability of the proposed method, calibration curves were plotted using 8 spiked levels of the analyte (0.5, 5.0, 10, 30, 50, 75 and 100 µg L^{-1}). Each standard sample was digested by the proposed method using the optimum conditions. For each level, three replicate digestions were conducted. The limit of detection (LOD), based on the signal-to-noise ratio (S/N) of 3, the regression coefficient (r^2), the linear range (LR) and the relative standard deviation (RSD) were calculated. Extraction recovery of spiked samples was in the range of 96-105%. A linear calibration graph was obtained in the range of 0.5-100 µg L^{-1} with regression coefficient corresponding to 0.996. The RSD for the determination of 10 µg L^{-1} Pd (II) was 3.5 % ($n = 10$), while LOD was 0.045 µg L^{-1}.

Influence of interfering ions

In view of the high selectivity provided by ET-AAS, the only interference may be attributed to the preconcentration step, in which the cations may react with PAN that may lead to a decrease in extraction efficiency. So, interference of co-existing ions on the preconcentration of Pd^{2+} was investigated. For the study of the interferences, the effect of interfering ions at different concentration ratio on the absorbance of a solution containing 10 µg L^{-1} of the analyte was studied. The tolerance limits of the indicated ions are the limits, which do not affect the analyte signal by more than 5%. Among the ions tested; Cl^-, NO_3^-, CO_3^{2-}, Na^+, K^+, PO_4^{3-}, F^-, Mg^{2+}, $CH_3CO_2^-$, $C_2O_4^{2-}$, $C_{10}H_{14}O_8^{2-}$, SO_4^{2-}, SCN^-, Ir^{2+}, Pt^{4+}, Au^{3+}, Rh^{3+} did not interfere even at concentrations 1500 times higher than of the analyte. However, as shown in the TABLE 3, Fe^{3+} and Fe^{2+} proved to interfere at concentrations higher than 25 times of the analyte. The interferences of Fe^{3+} were completely avoided by KF (8 × 10^{-4} M).

TABLE 3 : Tolerance limits of interfering ions in the determination of 10 μg L^{-1} of Pd^{+2}.

Tested ions	Tolerance limit (Ratio of interference concentration to Pd^{+2})
[Cl^-, NO_3^-, CO_3^{2-}, Na^+, K^+, PO_4^{3-}, F^-, Mg^{2+}, $CH_3CO_2^-$, $C_2O_4^{2-}$,	< 1500
$C_{10}H_{14}O_8^{2-}$, SO_4^{2-}, SCN^-, Ir^{3+}, Pt^{4+}, Au^{3+}, Rh^{3+}] Ag^+, Cr^{3+}	< 300
Ni^{2+}	< 200
Hg^{2+}, Al^{3+}, Cd^{2+}	< 150
Cu^{2+}	< 100
Fe^{3+}, Fe^{2+}, Co^{2+}	< 25

Analysis of road dust samples

The performance of this method was tested by analyzing the metal in the four different road dust samples. The results showed that the analyzed samples were free of Pd contamination. All of the real samples were spiked with the target metal standards at different concentration levels to assess the matrix effects. According to the TABLE 4, the added Pd (II) ions can be quantitatively recovered by the developed procedure. The accuracy of the method was tested by the recovery experiments on spiked samples with result ranging from 96-105%. These results demonstrate the suitable capability of the proposed method for determination of the analyte in different road dust samples with various matrices.

TABLE 4 : Results obtained for analysis of the target compounds in different dust samples.

Sample		Pd^{+2}
Hemmat highway (10.0 μg L^{-1} added)	Concentration (μg L^{-1})	Nd*
	Found (μg L^{-1})	9.6
	Recovery (%)	96
	RSD% (*n* = 10)	3.4
Hakim highway (20.0 μg L^{-1} added)	Concentration (μg L^{-1})	ND
	Found (μg L^{-1})	20.4
	Recovery (%)	102
	RSD% (*n* = 10)	3.3
Towhid tunnel (25.0 μg L^{-1} added)	Concentration (μg L^{-1})	ND
	Found (μg L^{-1})	26.1
	Recovery (%)	104
	RSD% (*n* = 10)	2.7
Azadi street (50.0 μg L^{-1} added)	Concentration (μg L^{-1})	ND
	Found (μg L^{-1})	52.5
	Recovery (%)	105
	RSD% (*n* = 10)	3.9

*** Nd: Not detected**

CONCLUSIONS

This paper outlines a successful development and application of a method using alumina-coated magnetite nanoparticles, combined with ET-AAS for the qualitative and quantitative analysis of Pd (II) in road dust samples. The results obtained demonstrate the applicability of the proposed procedure for preconcentration and traces determination of Pd^{+2} ions. The recoveries of analyte were nearly quantitative (> 96%). The developed method is simple, rapid, sensitive and also very suitable for screening of heavy metals on road dust samples.

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