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Graphite furnace-atomic absorption spectrophotometric determination of palladium in soil

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Abstract A new and sensitive procedure for the graphite furnace-atomic absorption spectrophotometric (GF-AAS) determination of Pd in soil at nanogram level is described. The method is based on prior separation and enrichment of the metal as Pd(II)-SnCl₃⁻-N-butylacetamide (BAA) complex into 1-pentanol (PN) by solvent extraction method. The value of the molar absorptivity of the complex in three solvents, i.e. ethyl acetate, 1-pentanol, chloroform, lie in the range of $(0.70\text{--}2.75) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 360–440 nm. The metal could be enriched into organic solvent, i.e. PN, up to 10-folds. The sensitivity ($A = 0.0044$) of the method in the term of the peak height was 0.5 ng Pd/mL of the aqueous solution at an enrichment factor (EF) of 5. Optimization of analytical variables during enrichment and GF-AAS determination of the metal are discussed. The method has been applied for the analysis of Pd to soil samples derived from roads and highways in Germany.

Introduction

The platinum group metals (PGM), e.g. Pt, Pd, Rh, are used as automobile exhaust emission control catalyst in several countries, e.g. USA, Germany, France, UK, Japan, etc., and their levels in the environment are increasing [1]. The PGM compounds are not highly toxic but may cause contact allergies similar to Ni(II) [1–2]. Several sophisticated techniques, e.g. ICP-MS, ICP-AES, GF-AAS, NAA, etc., were used for the determination of Pd in soil samples [3–15]. Most of them need the prior separation and enrichment to avoid matrix interference and to enhance sen-

sitivity, e.g. fire assay, solvent extraction, ion-exchange. Therefore, in this work, tin(II)chloride and N-butylacetamide were used as reagents for the prior separation and enrichment of Pd into 1-pentanol for the GF-AAS determination in soil at ng-levels. Optimization of the analytical variables for the GF-AAS determination of the metal in soil is discussed.

Experimental

Reagents. All reagents used were analytical reagent grade (E. Merck). The standard solution of Pd (500 mg/L) was prepared by dissolving 0.209 g PdCl₂ (E. Merck, 59.85% Pd) in 90 mL HCl (11.5 M) and diluted to 250 mL with de-ionized water. N-Butylacetamide (BAA) was synthesized by the condensation of acetic anhydride with N-butylamine as described in [16]. A 5%, w/v (0.26 M) tin(II) chloride solution in 6 M HCl containing 1%, w/v (0.07 M) hydrazine sulfate was used for the reduction and complexation of the metal. A 6%, w/v (0.5 M) BAA solution in 1-pentanol was used for extraction of the stannous-complex.

Instrumentation and operating conditions of GF-AAS. The Perkin-Elmer 4100-ZL atomic absorption spectrophotometer, a Perkin-Elmer THGA graphite furnace (equipped with a Zeeman-AA background correction system), and a Perkin-Elmer AS-70 autosampler were used for palladium measurement. The lamp current was adjusted to 30 mA, the used wavelength was 247.6 nm, the slit width was 0.7 nm, the injection volume was optimized to 20 μL , as measurement mode the peak area was evaluated and the integration time was 2 s. The graphite furnace temperature programs are summarized in Table 1.

Table 1 Graphite furnace temperature programs for measurement of Pd

Program	Temperature (°C)	Ramp (sec)	Hold (sec)	Ar flow (mL min ⁻¹)
Drying-I	110	1	20	250
Drying-II	130	5	30	250
Charring	900	10	20	250
Atomization	2200	0	5	0
Cleaning	2400	1	2	250

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Sample collection and digestion. Three surface soil samples were taken at roads and highways near Darmstadt, Germany. The surface soil (10 × 10 × 0–5 cm) was collected in August 1998 at the road no.26 (parking area at km 5 in eastern direction) and under the bridge of the highway's no. 5 and 67 crossing. The soil samples were dried, crushed and sieved to a particle size < 125 µm. 5.0 g of each sample was digested in a 250 mL Teflon beaker with 25 mL of freshly prepared aqua regia twice. The dried mass was heated with 5 mL HF to almost dryness. The residue was heated with 5 mL conc. HCl to remove HNO₃. Finally, it was dissolved with 10 mL HCl acid (4 M) and filtered by Whatmann filter paper no.42 to remove suspended particles. The filtrate was diluted to 15 mL with HCl acid (4 M).

Procedure for determination of Pd. 15 mL aliquot of each soil extract in three different separatory funnels (125 mL) were taken and spiked with 0.15, 0.24, and 0.36 µg Pd. The aqueous solution was allowed to react with 0.5 mL tin(II) chloride solution containing hydrazine sulfate for 1 min, and equilibrated with 3.0 mL PN solution of BAA for 1 min. The extract was transferred into a polyethylene tube. Similarly, the reagent blank was prepared. A 20 µL aliquot of the extract and the reagent blank in triplicate were injected into the graphite furnace of AAS for the determination. The Pd content present in soil extract was determined by standard spike method.

Results and discussion

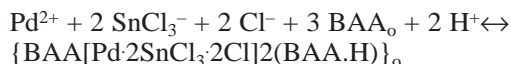
Liquid – liquid extraction and spectral characteristics

In strong HCl solution, tin(II) chloride reacts at room temperature with Pd(II) to give a yellow colored stannocomplex. The complex was partially extractable into polar organic solvent, i.e. 1-pentanol (PN), ethyl acetate (EA). The use of amides, e.g. BAA, in the polar organic solvent remarkably enhanced the distribution ratio of the metal (e.g. > 1500-folds into PN). However, the color of the complex is unstable (for at least 5 min) in EA. In non-polar organic solvent, i.e. chloroform (CF), carbon tetrachloride, benzene, toluene, the complex was extractable only in the presence of the amide, but oily droplets appeared at the interface of both phases in the case of aromatic hydrocarbons and carbon tetrachloride. Solvent, i.e. PN, EA, CF, quantitatively extracted the metal in the presence of BAA. The complex showed a sharp λ_{\max} around 420–440 nm in these solvents, however, in the CF, two λ_{\max} appeared at 360 and 440 nm. The spectral data of the complex in the various organic solvents are summarized in Table 2. The most sensitive color reaction was observed in EA, but the color of the complex was least stable (i.e. 5 min). In this work, 1-pentanol was selected for separation and enrichment of Pd due to high color stability (the color was sta-

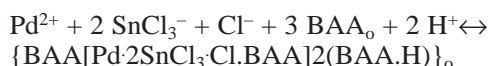
ble for at least 2 h at room temperature, 22 ± 2 °C) of the complex, relatively less volatility (than EA and CF) and lower miscibility (than EA) and lower toxicity (than CF). Acids, e.g. HCl, H₂SO₄, were tested for the extraction of the Pd(II)-SnCl₃⁻-BAA complex. Sulfuric acid could not be used due to very poor extraction of the metal (unextractable sulfato complex?). Optimum acidity range to get maximum and constant peak area or height of the analyte (≥ 98% extraction of the metal) for the GF-AAS determination was 3.0–6.0 M HCl. Beyond these limits, the distribution of the metal decreased either due to lower extraction or higher miscibility of the solvent.

Amides (e.g. N-phenylacetamide, N-butylacetamide, N-pentylacetamide, N-hexylbutamide, N-octylacetamide) derived by condensation of acetic anhydride with aliphatic and aromatic amines (i.e. butyl to octyl, phenyl) were found to enhance the distribution ratio of the metal (> 1000-fold). However, substitution of CH₃ in the aryl group at C-atom of the amide (e.g. N-phenylbenzamide, N-4-methylphenylbenzamide) or introduction of Cl-group in the phenyl ring at N-atom of the amide (e.g. N-2/3/4-chlorophenylacetamides) remarkably suppressed the extraction, may be due to the –I(inductive) effect as well as the strongly reduced solubility of the substituted amide into PN.

The composition of the complex was determined by the curve-fitting method by plotting distribution ratio (D) of the metal versus the molar concentration of the reagent used in a double-logarithmic scale. The slope for the curve log D vs log [SnCl₂] and log D vs log [BAA] was found to be 1.8 and 2.9, close to integer 2 and 3, respectively. The mole ratio of Pd:SnCl₃⁻:BAA in the extracted complex was assumed to be 1:2:3. The extraction procedure for the solvated complex can be written as:



or



The subscript “o” denotes to the organic phase. The role of BAA is assumed as counter ion as well as adductant or ligand. It remarkably increased the distribution ratio of the metal (> 1500-fold) into PN.

Effect of reagent concentration and other variables

The effect of reagent concentration on the extraction of the metal was examined. At least 8.0 × 10⁻³ M tin(II) chloride was required to get maximum and constant peak height of the signal and further addition of up to 2.5 × 10⁻² M did not cause adverse effect. Its addition, > 2.5 × 10⁻² M, increased gradually the background height of intensity signal and may be increasing co-extraction of tin ions. Therefore, no higher concentrations were applied. Up to the value of 2.5 × 10⁻³ M SnCl₂ no loss of Pd was observed. Hydrazine sulfate was used as the buffer to re-

Table 2 Spectral data of the Pd(II)-SnCl₃⁻-BAA complex in organic solvent

Solvent	λ_{\max} , nm	ϵ , L mol ⁻¹ cm ⁻¹
1-Pentanol(PN)	420	7,000
Ethyl acetate(EA)	430	27,500
Chloroform(CF)	440	9,500
	360	19,500

duce any stannic ions formed in situ in order for preventing hydrolysis of Sn(IV). Addition of hydrazine sulfate up to 1%, w/v (0.07 M) had no adverse effect. At least, 0.34 M BAA in PN was required for getting maximum and constant peak height of the signal and further addition up to 0.7 M had no adverse effect in the extraction. An equilibration period of 1 min was sufficient for the complete extraction of the metal and prolonged equilibration up to 5 min did not change the extraction. The extraction of the metal was not affected when the temperature of the aqueous solution was varied from 10–45 °C. Addition of strong electrolytes, e.g. KCl up to 1 M, into the aqueous phase did not change the distribution of the metal.

Enrichment of Pd

All solutions used were pre-saturated with PN. The enrichment (preconcentration) factor (C_{org}/C_{aq}) of Pd was determined by taking the same amount of Pd (0.45 µg) in 6, 9, 12, 15, 21, 27, 30, 33 mL, resp., of the aqueous solution at 4 M HCl containing 2.5×10^{-2} M tin(II)chloride + 4.6×10^{-3} M hydrazine sulfate. The aqueous solution was equilibrated with 3.0 mL of PN solution of BAA. The organic extract was separated and transferred into polyethylene tube for the GF-AAS injection. The maximum and constant extraction ($\geq 98\%$) of the metal was observed when the volume ratio of the aqueous to the organic phase lies between 1 : 1 and 1 : 10. It means Pd was enriched into the PN solution maximum up to 10-fold and beyond it, the extraction was decreased, may be due to lower distribution of the BAA in the organic solution.

Effect of diverse ions

The effect of diverse ions in the GF-AAS determination of 20 ng Pd/mL (in aqueous solution) was examined. A 15 mL aliquot of Pd (20 ng/mL) solution contaminated with different amounts of diverse ions (µg/mL) at 4 M HCl + 2.0×10^{-2} M SnCl₂ + 4.6×10^{-3} M hydrazine sulfate was extracted with 3.0 mL PN solution of BAA as described in the procedure. The extract was allowed for GF-AAS injection using the appropriate reagent blank. Addition of more diverse ions beyond tolerable amounts caused either positive or negative deviation, may be due to co-extraction or co-precipitation/adsorption. The tolerable amounts (in µg/mL) of diverse ions are summarized in Table 3.

Optimum concentration range, precision and sensitivity

The mean background peak area and height were 0.001 and 0.005, respectively. The mean ($n = 3$) background corrected peak area/height for 10.0, 20.0 and 30.0 ng Pd/mL of the aqueous solution (or 50.0, 100 and 150 ng/mL Pd in PN) were 0.060/0.088, 0.115/0.165 and 0.175/0.234, respectively. The calibration curve plotted between the background corrected peak area/height versus concentra-

Table 3 Effect of diverse ions in the GF-AAS determination of 20 ng Pd/mL of the aqueous solution

Ion added	Concentration of ion, µg/mL	Remark
Al(III), V(V), Mn(II), As(V), Mo(VI)	50	Addition of more ion caused positive deviation both in BGSPH and ASPH
Cr(III)	60	
Cr(VI)	20	
Mn(VII)	15	
Fe(II)	200	
Fe(III)	100	
Co(II), Ni(II)	25	
Cu(II)	15	
Zn(II), Tl(III)	25	
Pb(II)	30	
Ti(IV)	40	Addition of more ion caused negative deviation in ASPH
Se(IV), Ag(I), Hg(II)	2	
Bi(III)	20	
Borate, oxalate, EDTA	1000	

ASPH = analyte signal peak height; BGSPH = background signal peak height

tion, e.g. 50.0, 100 and 150 ng/mL Pd, was found to be linear with slope and co-relation coefficient of 0.0012 and +0.999, respectively. The sensitivity in the term of peak height (amount causing 0.0044 A) of the method was determined and found to be 0.5 ng Pd/mL of the aqueous solution. The relative standard deviation of the method at the level of 20 ng Pd/mL of the aqueous solution ($n = 3$) was $\pm 2.6\%$.

Application

Three soil samples taken at roads and highways near Darmstadt, Germany, were analyzed as described in the procedure and found to be Pd-contaminated with 58.6 ± 4.9 ng/g soil, 11.0 ± 2.1 ng/g soil, and 7.2 ± 0.9 ng/g soil, respectively. The standard deviations were calculated from 3 separate determinations each. The validity and reliability of the results was proven by measurements performed at the same time by GF-AAS in a comparison study of soils, which were treated ecologically and conventionally, respectively [17, 18]. The Pd contamination in Dieburg is lower than in San Diego, USA, where it amounts to 300 ng Pd/g [3].

Conclusions

Among various organic solvents (e.g. 1-pentanol, ethyl acetate, chloroform) tested for the GF-AAS injection, 1-pentanol was found to be the best diluent due to higher extractability and lower miscibility, volatility or toxicity. Similarly, all extractants claimed for the extraction-spec-

trophotometric determination of Pd could be used for the separation and enrichment of Pd for the GF-AAS determination. In addition, the prior separation with solvent extraction procedure reduced the background peak height, may be due to less matrix interference. The selectivity and enrichment of the method could be remarkably enhanced by prior separating the metal with a ligand/chelating agent of high organophilic character complexing the metal in the moderate acidic solution.

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