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# Selective separation of palladium (II) from precious metal ions using thiosemicarbazone derivatives from acidic media by solid phase and solvent extractions

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## ABSTRACT

A newly reported chelating ligand, 9,10-phenanthraquinone ethylthiosemicarbazone (PET), has been used for selective separation of Pd(II) by solid phase extraction (SPE) and solvent extraction (SE) in highly acidic media. PET was chemically immobilized on aminopropylsilica gel, yielding PET-SG, and complexes of PET and PET-SG with Pd(II) were synthesized and confirmed by IR, UV, thermal and elemental analyses. Free PET forms a 1:1 complexwith Pd(II) in solution with a stability constant of $3.5 \times 10^8$ and ε of $2.5 \times 10^5$ $dm^{-3}\,mol^{-1}\,cm^{-1}$ those were determined spectrophotometrically at 605 nm. PET-Pd(II) shows a superior stability in concentrated $H_2SO_4$, $H_3PO_4$, $HNO_3$, $HClO_4$ and glacial acetic acids for at least 24 h. It is easily and quantitatively extractable (%E = 99.6) in a one-stage process into MIBK from 10 mol/$dm^3$ $H_2SO_4$. PET-SG has a Pd-uptake capacity of 0.31 mmol/g and found to be stable in saline liquors from pH 8 to 2 mol/$dm^3$ $H_2SO_4$ or equivalent acidity of the studied acids. Leaching of >99.7% of Pd(II) was possible from 0.5 mol/$dm^3$ $H_2SO_4$ without interferences except for thiosulphate and thiourea, so 0.5% thiourea in 1 mol/$dm^3$ HCl was used as an eluent for stripping of Pd uptake in SPE and SE. SPE and SE techniques were applied for Pd(II) separation and preconcentration from various samples containing Pt(II;IV), Ag(I), Au(III) and Rh(III) followed by FAAS.

*Keywords*: Palladium; Silica gel; Solid phase extraction; Phenanthraquinone ethylthiosemicarbazone

## 1. Introduction

Noble metals, particularly palladium, find extensive use in jewellery, electrical industry, electronics, electrodes and chemical apparatus [1–4]. Further, there is also much current interest in the use of palladium in fuel cells as a catalyst [5] and in antipollution devices for automobile high-technology applications [1,4]. The need of Pd metal is upsoaring and the practice of its selective separation, recovery and refining is becoming increasingly important. Its recycling from waste materials has been seen particularly as one of the most promising technologies for the future as scraps of electronic devices that may contain more palladium than in some geological minerals [6].

As a result of increasing recent uses of palladium, it enters the environment *via* abrasion and deterioration which lately may be accumulated in living organisms jeopardizing life [7]. Some of Pd compounds have been reported as human allergens [1]. Although the concentration of Pd in different compartments of environment

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continuously increases, it is still at the level of ng/g [1,7]. This range is undetectable with conventional techniques such as FAAS and spectrophotometry owing to insufficient sensitivity and matrix interferences indicating that a preliminary separation and preconcentration is inevitable [8]. Therefore, selective separation and preconcentration of Pd(II) are necessary for metallurgical as well as analytical purposes prior to its determination even with sensitive techniques such as ICP-AES [9,10], ICP-MS [11,12] and GF-AAS [13,14].

Different techniques have been introduced for separation of Pd from interfering matrix such as co-precipitation [15,16] and electrochemical preconcentration [17,18]. Solvent extraction [8, 19–21] and solid phase extraction (SPE) [9,10,22–24] have been considered as the most effective techniques for recovery and separation of palladium since the classical precipitation method appeared to be an inefficient separation process. However, the most common methods of Pd extraction from acid media as negatively charged chloro complexes into organic solvents or anionic ion exchanger are tedious, less selective and long processes [19,20, 25]. Selectivity improvement may be achieved by the use of chelating sorbents with dithio and thio functional groups [20,21] or nitrogen-containing ligands [26]. The main difficulties in this method are its slow kinetics of formation of the extractable species from the starting chloro complexes and inadequate selectivity in respect to other precious metal ions. SPE is preferred over solvent extraction due to higher concentration factor and avoiding toxic solvents. Different supports such as biosorbents [27,28], polyurethane foam [29], activated carbon [30,31], and various silica forms [9,32–35] were applied in SPE after immobilization of function groups such as bis(carboxymethyl)dithiocarbamate [35,36], dithizone [37], thiosemicarbazide [38], 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) [39], Pd(II)-imprinted aminopropyl [10] and N-(3-triethoxysilylpropyl)- 4,5-dihydroimidazole [34]. In particular, materials whose surfaces have been functionalized with groups containing sulfur and nitrogen as active donor atoms have high selectivity for platinum metals [26].

In [40], PET was introduced as a new chromogenic reagent for the spectrophotometric determination of Tl [I; III] prior to its separation and preconcentration by SPE on polyurethane foam or flotation using oleic acid/kerosene as a surfactant.

For this purpose, the aim of the present work is to introduce PET to produce a new sorbent that has S and N as active donor atoms and its application as a selective extractor of Pd(II) using SPE based on amino silica gel and SE in methyl isobutyl ketone (MIBK) from highly acidic media in the presence of precious metal ions and determination of palladium by flame atomic absorption spectrometry (FAAS).

## 2. Experimental

### 2. 1. Materials

Unless otherwise specified, all chemicals used were of analytical reagent grade and were used without further treatment as received from suppliers (http://uk.vwr.com/ and http://www.sigmaaldrich.com). Doubly distilled water (DDW) was used throughout. PET (structure 1) was synthesized as reported previously [40] and a stock solution of $1 \times 10^{-3}$ mol/dm$^3$ in MIBK for spectrophotometric studies and solvent extraction was used in all subsequent studies.

Stock solution of Pd(II) (1000 mg/dm$^3$) was prepared by dissolving the appropriate amount of palladium chloride with 0.1 mol/dm$^3$ HCl in methanol. Working solutions were prepared from the stock solution by appropriate dilutions with DDW.

PET-SG was synthesized by refluxing 1.5 g of PET with 10 g of aminopropylsilica gel (APSG) from Fluka (capacity 0.9 ± 0.1 mmol/g) in dimethylformamide over an oil bath with continuous stirring at 120°C. The capacity of PET-SG (11 g yield) was found to be 0.31 mmol PET/g as obtained from the loss of PET concentration in the filtrate at 445 nm.

Pd(II) complexes, (Pd-PET) and (Pd-PET-SG), were synthesized by refluxing 100 cm$^3$ of 1000 µg/cm$^3$ Pd(II) (acidified with 1 cm$^3$ concentrated HCl) and 0.29 g of PET dissolved in a little amount of acetone or 3.03 g PET-SG, over a water bath for 2 h. Olive green products (0.38 g of Pd- PET or 3.1 g of Pd-PET-SG) were developed which filtered, washed with ethanol followed by diethyl ether and stored on a vacuum desiccator over dry $CaCl_2$. Pd content was determined by FAAS, after cautious ignition up to 800°C of the complex rolled with sodium metal then dissolved in aqua regia. Chloride content was gravimetrically determined as AgCl. The main characteristic features of the compounds formed are presented in Table 1.

### 2.2. Apparatus

Spectrophotometric studies were recorded on Unicam UV 2100 UV/Vis. while IR spectral analyses were performed for KBr disks using Mattson 5000 FTIR spectrophotometer with optimum conditions (resolution 4 cm$^{-1}$ ; Scan No. 40 and disk pressure 10 ton/cm$^2$) and the instrument was calibrated using polystyreen film. pH values of all solutions were measured using a Hanna instrument 8519 digital pH-meter using 2 mol/dm$^3$ $H_2SO_4$ and 2 mol/dm$^3$ NaOH for controlling the pH. Atomic absorption measurement of Pd(II) was recorded using a Perkin-Elmer 2380 atomic absorption spectrometer with an air-acetylene flame. Absorbance was measured at 276.3 nm at a spectral band pass of 0.2 nm. An

Table 1
Elemental analysis of PET, PET-SG, Pd-PET and Pd-PET-SG.

| Compound | | C% | H% | N% | S% | Cl% | Pd% |
|---|---|---|---|---|---|---|---|
| PET | Calculated | 66.00 | 4.89 | 13.58 | 10.36 | – | – |
| | Found | 66.17 | 4.88 | 13.45 | 10.12 | – | – |
| Pd-PET | Calculated | 41.95 | 3.11 | 8.63 | 6.59 | 14.57 | 21.86 |
| | Found | 41.82 | 3.05 | 8.70 | 6.59 | 14.55 | 21.89 |
| PET-SG | Calculated* | 7.45 | 0.66 | 1.30 | 0.99 | – | – |
| | Found | 8.59 | 0.94 | 1.71 | 0.99 | – | – |
| Pd-PET-SG | Calculated* | 4.95 | 0.44 | 0.87 | 0.66 | 1.46 | 2.19 |
| | Found | 5.98 | 0.67 | 1.24 | 0.67 | 1.55 | 2.32 |

*Values calculated according to the data of spectrophotometric determination (0.31 mmol PET/g).

automatic VARIO EL ELEMENTAR instrument was used to determine the percentage of C, H, N and S. Analysis of Si was performed by a SPECTRO CIROS CCD Inductively Coupled Plasma-Optical Emission Spectrometer. Emission lines at 212.412, 251.612 and 288.158 nm respectively were used to detect Si, whereas Ar lines at 404.442 and 430.01 nm were used to observe the stability of the generated plasma. Thermogravimetric analysis (TGA) of the modified silica gels was carried out using a Shimadzu thermobalance using a heating rate of 10°C/min in a purified $N_2$ atmosphere. Proton-nuclear magnetic resonance ($^1$H-NMR) measurement was performed for PET in $CDCl_3$ using a JEOL 270 EX-spectrometer.

### 2.3. Procedure

All experiments were carried out at ambient temperature and pressure.

*Spectral detection:* To determine the concentration of Pd(II) spectrophotometrically, an aliquot of a sample solution containing 2-100 µg of Pd(II) was added to 25 cm$^3$ of 5 mol/dm$^3$ $H_2SO_4$ in a 100 cm$^3$ separating funnel followed by adding 2 cm$^3$ of $1 \times 10^{-3}$ mol/dm$^3$ PET in MIBK and the solution was shacked very will then left to settle. After that, a suitable volume of the organic layer was transferred to a 1-cm glass cell and the absorbance was measured at 605 nm against the reagent blank. For FAAS measurements, the organic phase was aspirated directly without elution into the flame and the signals related to Pd(II) concentration were recorded at 267.3 nm.

*Solvent Extraction:* 10 cm$^3$ of 0.1–$5 \times 10^{-5}$ mol/dm$^3$ PET in MIBK was vigorously shaken with 500 cm$^3$ of 0.1–5 $\times 10^{-6}$ mol/dm$^3$ Pd(II) and media was adjusted to acidity of 5 mol/dm$^3$ $H_2SO_4$ in a 1000 cm$^3$ separation funnel for 10 min. The mixture was left to settle for 5 min (optimized time) to ensure complete separation of the olive green organic layer which was separated, and directly aspirated for determination of Pd(II) by FAAS. The effect of temperature and foreign ions was similarly studied. The distribution ratio, *D*, was calculated as the concentration of palladium present in the organic phase to that part in the aqueous phase at equilibrium according to equation (1):

$$D = \frac{\text{Pd(II) concentration in MIBK (mg/dm}^3)}{\text{Pd(II) concentration in aqueous layer (mg/dm}^3)} \tag{1}$$

From *D* values, the percentage extraction (%*E*) was calculated using equation (2) [41]:

$$\text{Percentage extraction (\%}E) = 100 \times \frac{D_{pd}}{D_{pd} + (V_{aq}/V_{org})} \tag{2}$$

where $V_{aq}$ and $V_{org}$ are the volumes of aqueous and organic phases.

*Batch mode solid phase extraction with PET-SG:* A total of 50 mg of PET-SG was suspended with constant stirring for 30 min in 50 cm$^3$ of 20 µg/cm$^3$ of Pd(II) at the desired acidity of $H_2SO_4$ or pH values. The residual concentration of Pd(II) in the filtrates was determined by FAAS and distribution coefficient ($K_d$) was determined using equation (3):

$$K_d = \frac{C_{\text{i.ex.}(\mu g/g)}}{C_{\text{sol}(\mu g/cm^3)}} \text{cm}^3/\text{g} \tag{3}$$

where $C_{\text{i.ex}}$ is the metal concentration in the solid phase and $C_{\text{sol}}$ is its concentration in the solution phase.

Effect of stirring time was studied at acidity 0.5 mol/dm$^3$ $H_2SO_4$ using the same conditions applied previously then the optimum conditions; 0.5 mol/dm$^3$ $H_2SO_4$, time of stirring = 10 min and weight of PET-SG = 25 mg;

were applied for studying the effect of interfering ions and eluting solution.

Pd(II) capacity of PET-SG was determined by adding 100 mg of the sorbent to 100 $cm^3$ of 100 µg/$cm^3$ of Pd(II) as chloride solution followed by stirring for 60 min and the acidity was adjusted. The suspension was filtered and the capacity was determined from the loss of metal concentration in the filtrate according to equation (4):

$$Capacity = \frac{100 - concentration\ of\ solution\ after\ extraction_{(\mu g/cm^3)}}{106.4}\ \text{mmole Pd/g} \tag{4}$$

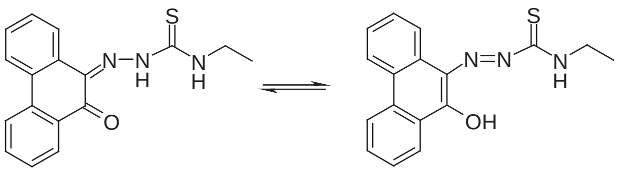
Stability of silica phases in aqueous solution was investigated by adding 100 mg of PET-SG to 200 $cm^3$ of distilled water adjusted to acidity of 0.5 mol/$dm^3$ $H_2SO_4$ under continuous stirring for 24 h. Aliquots of 6 $cm^3$ were withdrawn with a syringe through a diaphragm membrane with pore size of 0.20 µm type PET-20/25 from MACHEREY–NAGEL and hydrolyzed Si was determined by ICP-OES.

### 2.4. Determination of palladium (II) in spiked natural and scrap samples

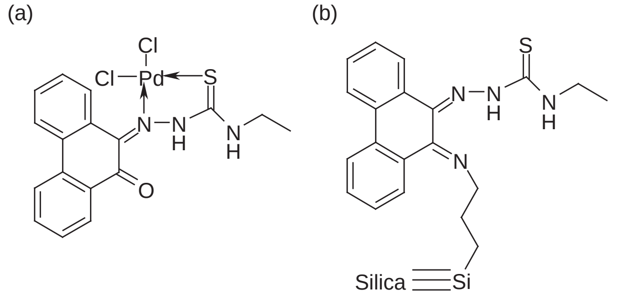
For determination of Pd(II) in seawater sample from Suez Bay, an aliquot of 500 $cm^3$ filtered sample was spiked with 2.5 and 5.0 µg of Pd(II) and the sample acidity was adjusted to 0.5 mol/$dm^3$ $H_2SO_4$. FAAS determination was attained after separation and preconcentration with both the SE (5 $cm^3$ of 5 × $10^{-5}$ mol/$dm^3$ PET in MIBK was shaken for 10 min and settled for 5 min) and SPE (50 mg of PET-SG in two batches, time of stirring was 10 min and eluent was 5 $cm^3$ 0.5% thiourea in 2 mol/$dm^3$ HCl).

Determination of Pd(II) in bronze coin (25 piaster) was similarly performed. A weight of 3.51 g of the coin was dissolved in aqua regia till near dryness then spiked with 2.5 and 5.0 µg of Pd (II), adjusted to acidity 0.5 mol/$dm^3$ $H_2SO_4$ and the total volume was completed to 500 $cm^3$. SE and SPE techniques were again applied on the samples as described above.

Determination of Pd(II) in silver and Pt scraps (90.18 and 1.45% respectively) from a jewellery workshop was performed. A weight of 1.0 g of each scrap was heated in concentrated $HNO_3$ till complete dissolution then heated near dryness, the residue was discarded and the clear solution was spiked with 2.5 and 5.0 µg of Pd (II). The mixture was adjusted to acidity of 1 mol/$dm_3$ $HNO_3$ (replacing $H_2SO_4$) and the volume was completed to 500 $cm^3$. SE and SPE techniques were again applied on the samples as described above.



Scheme 1. Ket-enol tautomerism of 9,10-phenanthaquinone monoethylthiosemicarbazone (PET)



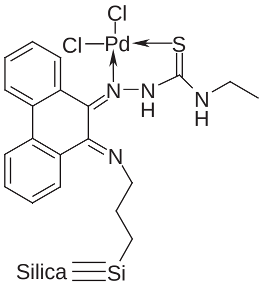
Scheme 2. 1:1 complex of Pd(II) with PET (a) and PET-SG (b).

## 3. Results and discussion

### 3.1. Characterisation of PET, PET-SG and their Pd(II) complexes

IR spectrum of PET shows strong bands at 764 and 1673 $cm^{-1}$, shoulders at 1560, 1635 $cm^{-1}$ and a broad band at 3400 $cm^{-1}$ assigned to $\nu_{C=S}$, $\nu_{C=O}$, $\nu_{C=N}$, $\nu_{N=N}$ and $\nu_{OH}$, respectively. Its $^1H$ NMR $CDCl_3$ suggests the presence of aromatic protons as multiplet at $\delta = 7.5 - 8.2$ ppm, $CH_2$ as multiplet at $\delta = 3.85$ ppm, $CH_3$ as triplet at $\delta = 1.5$ ppm and O-H as singlet signal at $\delta = 14.5$ ppm. From these results and the elemental analysis, a keto-enol tautomerism of the phenanthraquinone moiety was confirmed (Scheme 1) [40].

The solid complex formed between PET and Pd(II) is olive green in color with a melting point of >300°C. Elemental analysis (Table 1) indicates the formation of 1:1 [Pd(II):PET] ratio with an empirical formula of $Pd(PET)Cl_2$. Thermal analysis of $Pd(PET)Cl_2$ shows three steps of degradation at 294, 470 and 680°C with a total weight loss of 71.2% at 800°C which is close to elemental analysis results . Careful comparison between IR spectrum of $Pd(PET)Cl_2$ and that of PET shows that PET acts as a bidentate ligand in the keto form coordinating *via* C=N and C=S (Scheme 2a). This mode of chelation is supported by: (i) disappearance of ν(N=N) and $\delta_{OH}$ bands; (ii) appearance of a new band at 330 $cm^{-1}$ assignable to ν(Pd–Cl) [42], (iii) bands assigned to ν(C=S) and ν(C=N) were shifted to 755 and 1534 $cm^{-1}$ and (iv) ν(C=O) band remains almost at the same position. From these results and those of elemental analysis, $Pd(PET)Cl_2$ complex is proposed (Scheme 3). It is sparingly soluble in ethanol



Scheme 3. Structure of PET-SG.

and methanol but easily soluble in acetone, MIBK, DMF or DMSO, with molar conductance indicating nonelectrolytic in nature.

Elemental analysis of PET-SG (Table 1) supports the immobilization capacity that found by spectrophotometric determination of the remaining PET concentration (0.31 mmol/g). Hydrogen content may be discarded due to the uncertainty of the amount of adsorbed water. It is clear from N% that one third of the initial APSG capacity is lost during further functionalization of silica and only 50% of the remaining aminopropyl capacity could be condensed with PET. This may be attributed to the steric hindrance of PET which is usually observed with bulky compounds [9,34,43–45]. IR absorption spectrum of PET-SG shows three bands at 1100–1200 (broad), 800 and 463 cm$^{-1}$ assigned to ν(Si-O), ν(Si-O-Si) and δ(Si-O-Si), respectively. Absorption band at 3400-3500 cm$^{-1}$ is corresponding to ν(OH). The band at 1640 cm$^{-1}$ may be overlapped bands mainly due to bending of molecular $H_2O$ and $SiO_2$ overtone. Bands at 3064 and 3189 cm$^{-1}$, assigned previously to ($\nu_s$) and ($\nu_{as}$) of $NH_2$ in the IR absorption spectrum of APSG [44,45] were not observed in the IR absorption spectrum of PET-SG. This means that this group is utilized in the condensation process as shown in Scheme (3).

PET-SG shows adequate stability in organic solvents e.g. DMF or DMSO and strong acids up to 2 mol/dm$^3$ $H_2SO_4$ or equivalent concentration of HCl, $H_3PO_4$ or $HNO_3$. Elemental analysis of Pd(PET-SG) confirms the same molar ratio observed in Pd-PET and they have the same olive green colour (Scheme 2b).

### 3.2. Spectrophotometric studies

PET may act as a monobasic acid in the enol form (Scheme 1). Its colour and maximum absorbance ($\lambda_{max}$) depends on the solution pH. The maximum absorbance at acidity 0.5 mol/dm$^3$ $H_2SO_4$ is 446 nm (Fig. 1) which represents the intramolecular absorbance of the unionized ligand in the keto form. The ligand is believed to be partially enolized as indicated from the small absorption peak at 414 nm. Pd(II) forms olive green complex with PET over a wide range of acidity from 10 mol/dm$^3$ $H_2SO_4$ and to a pH value of 4 with a maximum absorbance at 605 nm (Fig. 1) with a higher shift than that of the free ligand. Stability constant of the complex formed between PET and Pd(II) was calculated according to Harvey and Manning method [46]. It is 3.5 × 10$^8$ indicating high stability of the complex. Stoichiometry of Pd(II)-PET complex was determined by continuous variation Job method [47] indicating a 1:1 ratio [Pd(II):PET] that is in agreement with the elemental and thermal analyses data of the solid complex.

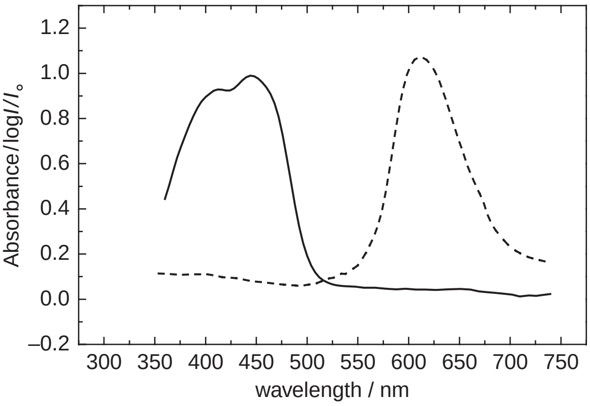


Fig. 1 Absorption spectra of PET in 0.5 mol/dm$^3$ $H_2SO_4$ vs. blank and in presence of Pd(II) vs. PET.

*Sensitivity and optimum conditions for spectrophotometric determination of Pd(II):* The colour development of Pd(II) with PET in various acid media, such as chloroacetic, glacial acetic, hydrochloric, nitric, sulphuric and phosphoric acids was investigated. The highest sensitivity was found in $H_2SO_4$ so it was used as medium in the determination. The maximum and linear absorbance could be obtained at acidity of 10 mol/dm$^3$ $H_2SO_4$ up to pH 4.0. The chromogenic reaction is completely developed within one minute at room temperature and the formed complex was stable for at least 24 h. Beer's law was obeyed over the concentration range of 0.1–10 μg/cm$^3$ of Pd(II).

The optimum concentration range for reliable determination of palladium ion in PET-MIBK (Ringbom plot) is between 0.07–0.15 μg/cm$^3$ Pd(II) in aqueous solution. Molar absorptivity (ε) of Pd(PET)$Cl_2$ complex in MIBK is found to be 2.5 × 10$^5$ dm$^3$/mol/cm comparing to Sandell's sensitivity index of 0.75 ng/cm$^2$ of Pd(II) and specific absorptivity (a) is found to be 0.23 cm$^3$/g/cm. Relative standard deviation (R.S.D) level for the determination of 10 replicate at 0.1 μg/cm$^3$ Pd(II) is 1.5 %

Pd(PET)$Cl_2$ shows a superior resistance to concentrated acids ($H_2SO_4$, $H_3PO_4$, $HNO_3$, $HClO_4$ and glacial AcOH) for at least 24 h. However, 6 mol/dm$^3$ HCl read-

Table 2
Determination of palladium (II) by spectrophotometric determination as its PET complex in 0.5 mol/dm³ $H_2SO_4$ compared with the standard FAAS in spiking sea water.

| Pd(II) added µg/ 100 cm³ | Palladium found µg/cm³ | | | | | | $\lvert t\rvert_2$ | $F$ |
|---|---|---|---|---|---|---|---|---|
| | Spectrophotometrically | | | FAAS | | | | |
| | $\bar{X}\pm\frac{ts}{\sqrt{n}}$ | RSD % | Recovery % | $\bar{X}\pm\frac{ts}{\sqrt{n}}$ | RSD % | Recovery % | | |
| 0.5 | 0.49±0.02 | 0.84 | 98.5 | 0.50±0.04 | 1.38 | 100.0 | 0.48 | 1.41 |
| 1.0 | 1.00±0.05 | 0.83 | 100.0 | 1.01±0.04 | 0.74 | 100.1 | 0.32 | 0.41 |
| 1.5 | 1.51±0.05 | 0.55 | 100.7 | 1.49±0.08 | 0.91 | 99.3 | 0.97 | 1.39 |
| 2.0 | 1.99±0.10 | 0.94 | 99.5 | 2.01±0.09 | 0.82 | 100.5 | 0.28 | 0.40 |
| 2.5 | 2.49±0.05 | 0.38 | 99.6 | 2.51±0.14 | 1.00 | 100.4 | 0.15 | 3.52 |

$\bar{X}$ = average value, $n$ = 5, $s$ = standard deviation, $t$ = student factor, $p$ = 0.05. RSD means relative standard deviation.

ily dissociates the complex, hence 5 mol/dm³ HCl is considered tolerant.

Spectrophotometric determination of seawater sample spiked with 0.5–2.5 µg/100 cm3 of Pd(II) with PET in MIBK in 0.5 mol/dm³ $H_2SO4$ (Table 2) shows a recovery of 99.5–100.2% of the initial concentration with relative standard deviation (R.S.D) of 0.38 – 0.94%. Data were statistically compared with those obtained from FAAS using null hypothesis of $\lvert t\rvert_2$ and two-tailed F-test respectively [48], for P = 0.05 and n = 10, to indicate that the spectrophotometric determination of Pd(II) using PET is accurate and precise.

*Effect of diverse ions:* In order to evaluate the suitability of the proposed method for spectrophotometric determination of Pd(II), the effect of some common ions was studied by adding different amounts of diverse ions to 1 µg/cm³ of Pd(II) solution in 5 mol/dm³ $H_2SO_4$ (Table 3). An error less than ±2% was considered to be tolerable. In spite of high tendency of PET to form complexes with a great number of metal ions, no interference from high salinity or macroamounts of many foreign ions (up to 1000 times of the concentration of Pd(II)) was detected at the given conditions as shown in Table 3). Owing to high acidity of the used reaction medium, the tolerable amounts of many elements were over the mg/cm³ range. Thiourea was found to compete strongly PET in Pd(II) complexation at concentration as low as 0.1% and with a thiourea concentration of 0.5% a complete masking of Pd(II) was observed.

Table 3
Effect of interfering ions on the spectrophotometric determination of Pd(II) (1 µg/cm³) using PET 2 × 10⁻⁴ mol/dm³ in 0.5 mol/dm³ $H_2SO_4$.

| Interfering ion | Tolerance limit |
|---|---|
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Mn^{2+}$, $Fe^{2+,3+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ag^{2+}$, $Cd^{2+}$, $Mo^{6+}$ (as $MoO_4^{--}$), $F^-$, $Cl^-$, $Br^-$, $NO_3^-$ | 1000 fold |
| $Au^{3+}$, $Os^{3+}$, $Ru^{2+,3+}$, $Pt^{2+,4+}$, $Rh^{3+}$, $Co^{2+}$, $Pb^{2+}$, $In^{3+}$, $Tl^+$, $Tl^{3+}$, $W^{6+}$ (as $WO_4^{--}$), tartarate | 500 |
| $ClO_3^-$, $BrO_3^-$, citrate | 100 |
| $SO_3^{--}$, $S_2O_3^{--}$, $SCN^-$, oxalate | 50 |
| Thiourea | 1 |

### 3.3. Solvent Extraction

*Effect of metal and ligand concentrations:* The effect of PET concentration (0.1–5 × $10^{-5}$ mol/dm³) on the extraction of 2 × $10^{-6}$ mol/dm³ Pd(II) was investigated in 0.5 mol/dm³ $H_2SO_4$. The obtained data indicated that complete extraction of Pd(II) is attained only if [PET] ≥ [Pd(II)] so, during the SE process an excess amount of PET was added. Furthermore, another series of experiments was conducted to extract different concentrations (0.1 – 5 × $10^{-6}$ mol/dm³) of Pd(II) using 5 × $10^{-5}$ mol/dm³ PET. Complete extraction (E% = 99.6 and D = 3950) was obtained when PET: Pd ratio is more than 1:1.

*Efficiency of extraction (E%) and the distribution ratio (D):* Extraction efficiency (E%) and distribution ratio for different concentrations of Pd(II) were computed. The obtained data indicated that up to 100 mg Pd(II) could be quantitatively separated using 1 × $10^{-3}$ mol/dm³ PET. Also, high E (approx. 100%) and D (3950) allowed the extraction of Pd(II) by a single step separation procedure. It deserves to mention that when the distribution ratio of a given element in a specified system is large (e.g. 1000, log D = 3), a single step extraction will suffice [49].

*Preconcentration factor:* To determine the preconcentration factor ($\alpha = V_{aq} / V_{org}$), trials were made to extract

$1 \times 10^{-6}$ mol/dm$^3$ of Pd(II) from 500 cm$^3$ aqueous solution using different volumes of $1 \times 10^{-3}$ mol/dm$^3$ PET in MIBK as a solvent. The obtained results indicated that the Pd(II) content in 500 cm$^3$ aqueous solution could be extracted completely using 5 cm$^3$ of MIBK. Moreover, it was noted that on extracting higher concentration of Pd (II), e.g. >0.5 µg cm$^3$, addition of sodium sulphate was useful for salting-out and preventing emulsification; the minimum quantity for reproducible results was 50 cm$^3$ of saturated sodium salt solution in 500 cm$^3$ of aqueous phase. The high preconcentration factor (>100) extremely enhanced the sensitivity of the proposed preconcentration procedure and permits the determination of Pd(II) in fraction of gram scale.

*Effect of temperature:* A series of experiments was conducted over a temperature range (20–80°C) to determine the proper temperature required for maximum extraction of Pd(II)-PET complex. It was found that SE process was not markedly affected in the temperature range of 20–60°C. Therefore, subsequent measurements were carried out at room temperature, i.e. 25°C.

*Stripping of palladium from loaded organic layer:* Stripping studies of Pd(II) from loaded organic phase containing 0.11 g/dm$^3$ Pd(II) were carried out in thiourea acidified with HCl acid in different concentrations followed by plenty washing with distilled water to use the PET-organic layer for another extraction experiments. Results indicated that stripping efficiency (100%) was obtained by using 5 cm$_3$ of 0.5% thioura in 2.0 mol/dm$^3$ HCl media that strip all the quantity of palladium content in PET-MIBK layer.

*Effect of foreign ions:* Similar to the effect of foreign ions discussed in spectrophotometry (Table 3), no interference was seen for all studied metal ions of periodic table and major organic and inorganic anions with Pd(II)-PET extraction in MIBK except for Tl(III), Ag(I), Bi(III) and Au(III) that interfered to some extent at pH ≥1.5 in the presence of $HNO_3$ acid, so acidity ≥ 0.5 mol/dm$^3$ $H_2SO_4$ or HCl will remove these interferences. Competition of Cl–$^-$ with PET at [HCl] ≥5 mol/dm$^3$ is confirmed (Fig. 2). Total Pd(II) extracted in MIBK is unaffected by the acid concentration and the complex formation begins to dissociate at [HCl] >5 mol/dm$^3$. This means that the dissociated part is also extracted in MIBK as chloro complex $[Pd(Cl)_4]^{2-}$ [20]. However, the presence of high concentration of Cl$^-$ is not favoured as it will affect the selectivity of the extraction procedure. This result is comparable to that obtained by Shen and Xue (>99.9% at pH 2) [8] using 2-hydroxy-4-sec-octanoyl diphenyl ketoxime diluted in kerosene in three-stages. However, the introduced method is preferred as it is achieved in one-stage and for the absence of interferences from precious metal ions at pH <1 and from concentrated acids except for HCl. Thiourea and thiosulphate seriously interfered in the extraction of palladium ion. Accordingly, 0.5% thiourea in 2 mol/dm$^3$ HCl was found to quantitatively leach back Pd(II) extracted in $5 \times 1$–$^5$ mol/dm$^3$ PET in MIBK which is an advantage for the recycling of ligand.

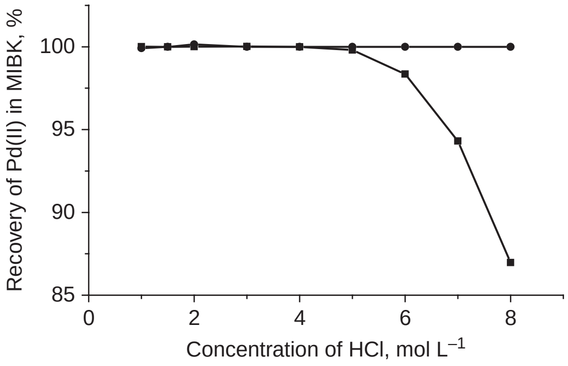


Fig. 2 Effect of concentration of HCl on the extraction of $5 \times 10^{-6}$ mol/dm$^3$ of Pd(II) in 500 cm$^3$ to 5 cm$^3$ MIBK. –•– = Pd(II)-PET complex determined by spectrophotometry and –•– = total Pd(II) determined by FAAS.

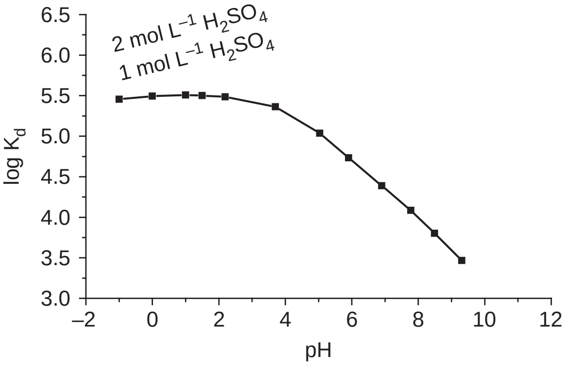


Fig. 3 Effect of acidity and pH on the extraction of 1.0 µg/cm$^3$ of Pd(II) in 50 cm$^3$ on 50 mg PET-SG after time of stirring 30 min.

### 3.4. Solid Phase Extraction (SPE)

Figure 3 shows the logarithmic value of distribution coefficient (log$K_d$) of Pd(II) on PET-SG versus pH using the batch-mode SPE. An efficient separation of Pd(II) has been observed from acidity of 2 mol/dm$^3$ $H_2SO_4$ to pH 8.0 giving log$K_d$ values of 5.50–4.97 corresponding to extraction efficiencies of 99.69%–98.94%, respectively. This long plateau of applicable acidity and pH values means that Pd(II) bonding with PET-SG is with no proton exchange which is in accordance with IR results of Pd-PET. In addition, this enables flexible choice of the

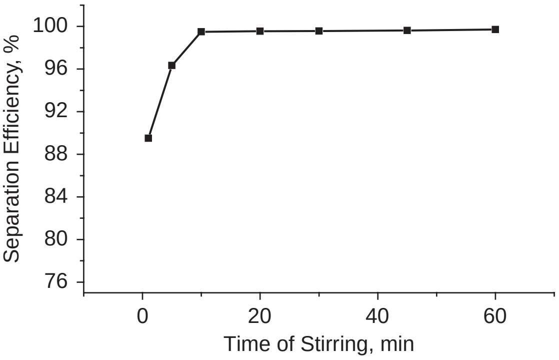


Fig. 4 Effect of time of stirring on the extraction efficiency of 1.0 µg/cm3 of Pd(II) in 50 cm$^3$ 0.5 mol/dm$^3$ $H_2SO_4$ using 50 mg PET-SG.

range of pH at which minimum interference may occur from other precious metal ions and to avoid basic region which causes hydrolysis to silica [50]. Acidity 0.5 mol/dm$^3$ $H_2SO_4$ was found to be optimal for avoiding interferences and obtaining high extraction efficiency of Pd(II) as well. However, similar tolerance of the spectrophotometry and SE to common ions was found in SPE. Moreover, thiourea or 6 mol/dm$^3$ HCl strongly interfered the SPE process of Pd(II) with PET-SG. For this reason, 5 cm$^3$ of 0.5% thiourea in 0.2 mol/dm$^3$ HCl were enough to elute 100% of the extracted Pd(II). Effect of time of stirring on separation efficiency of Pd(II) on PET-SG in 0.5 mol/dm$^3$ $H_2SO_4$ is shown in Fig. 4. It shows that at 10 min, separation of Pd(II) reaches its maximum value and still constant up to 60 min. The development of maximum equilibrium within the first 10 min of stirring is an advantage which may be due to fast chelation kinetics of PET and wide open structure of silica gel.

Maximum Pd(II) capacity of PET-SG was found to be 0.3 mmol/g (31.9 mg Pd/g) that is comparable to results of the elemental analysis and the ligand immobilization capacity suggesting 1:1 Pd:PET ratio just as in case of the free ligand. This Pd(II) capacity is appreciably higher than that obtained by Zheng et al. [10], 26.7 mg/g using imprinted-aminopropyl silica gel and Jamali et al. [9], 5.0 mg/g with thiophene-2-carbaldehyde immobilized on MCM-41. To examine stability of PET-SG against hydrolysis during the experimental conditions, the hydrolyzed Si was analyzed after 24 h which indicated the presence of negligible silica hydrolysis (1.61%).

### *3.5. Detection limit*

The instrumental detection limit $DL_i$ of Pd(II) determination by spectrophotometry, based on three times the standard deviation of the blank above its mean value, was 0.11 mg /dm$^3$. The blank was 10 cm$^3$ of $1 \times 10^{-4}$ mol/dm$^3$ PET in 50% acetone acedified with 0.5 mol/dm$^3$ $H_2SO_4$.

$DL_i$ of Pd(II) determination by FAAS after SE was performed in the blank. The blank was 50 cm$^3$ of $5 \times 10^{-5}$ mol/dm$^3$ PET in MIBK which vigorously shaken for 10 min with 500 cm$^3$ DDW and adjusted to acidity of 0.5 mol/dm$^3$ $H_2SO_4$ then kept to settle for 5 min in a separation funnel. After complete separation of the organic layer, it was evaporated to 5 cm$^3$ and directly aspirated in the flame and $DL_i$ was found to be 0.32 mg/dm$^3$.

$DL_i$ of Pd(II) determination by FAAS after SPE was performed in the blank that was 5 cm$^3$ 0.5% thiourea in 2 mol/dm$^3$ HCl (used to elute the Pd(II) background) extracted on two batches of 50 mg of PET-SG and stirred for 10 min in 500 cm$^3$ of 0.5 mol/dm$^3$ $H_2SO_4$. $DL_i$ was found to be 0.25 mg/dm$^3$.

Analytical detection limits $(DL)_a$ were calculated by dividing the instrumental detection limits by the preconcentration factor of SE and SPE techniques (100 fold) and they found to be 3.19 for SE and 2.53 ng/cm$^3$ for SPE.

### *3.6. Application and statistical evaluation of SE and SPE techniques*

The proposed SE and SPE procedures were applied for separation and preconcentration of Pd(II) from seawater, bronze coin and precious metal scraps spiked with

Table 4
FAAS determination of Pd(II) in spiked seawater, bronze coin and precious metal scraps after separation and preconcentration by SE and SPE using PET in MIBK or immobilized on SG.

| Sample | Palladium added (µg) | SE | | | SPE | | |
|---|---|---|---|---|---|---|---|
| | | Found µg | RSD (%) | $\|t\|_1$ | Found µg | RSD % | $\|t\|_1$ |
| Seawater | 2.5 | 2.49 | 1.87 | 0.62 | 2.49 | 1.79 | 0.53 |
| | 5.0 | 5.01 | 1.29 | 0.42 | 4.97 | 1.88 | 0.72 |
| Bronze coin | 2.5 | 2.51 | 1.99 | 0.40 | 2.52 | 1.72 | 0.78 |
| | 5.0 | 4.99 | 1.59 | 0.25 | 5.02 | 1.14 | 0.74 |
| Precious metal scraps | 2.5 | 2.51 | 1.72 | 0.36 | 2.52 | 1.47 | 0.91 |
| | 5.0 | 4.99 | 1.39 | 0.35 | 4.98 | 2.01 | 0.47 |

Table 5
Separation of Pd(II) in binary mixtures in both SPE and SE under optimum conditions.

| Metal ion | Ratio (Pd(II):M) | % recovery of Pd(II) | Separation factor $\beta = D_{Pd}/D_M$ |
|---|---|---|---|
| Pt (IV) | 1:100 | 99.8 | $5.2 \times 10^4$ |
| Ag(I) | 1:100 | 99.9 | $5.3 \times 10^4$ |
| Au(III) | 1:100 | 99.9 | $5.6 \times 10^4$ |
| Rh(III) | 1:100 | 99.8 | $5.1 \times 10^4$ |
| Cu(II) | 1:200 | 99.9 | $5.3 \times 10^4$ |
| Hg(II) | 1:200 | 99.9 | $5.5 \times 10^4$ |

2.5 or 5.0 μg Pd(II). Results, shown in Table 4, indicate that there is no significant difference between the spiked amount and those recovered by SE or SPE using PET in MIBK or PET immobilized on SG from the investigated samples. As expected no Pd(II) background could be detected. The reliability of SE and SPE techniques was statistically examined using null hypothesis of $|t|_1$ for $p = 0.05$ and $n = 10$. It was found that $|t|_1 = 0.25$–0.0.91 which is less than the tabulated value ($|t|_1 = 2.31$) [48]. This indicates that the two suggested methods of separation and preconcentration of Pd(II) are not subjected to random errors (i.e. precise).

### *3.7. Separation of palladium(II) from binary mixtures:*

Palladium(II) was selectively extracted from some precious and neighboring elements under the optimum separation conditions in binary mixtures (Table 5). Separation factor (β) was calculated as the ratio of the distribution ratio of palladium (II) to that of metal ion which was introduced in the mixture ($\beta = D_{Pd}/D_M$). In all these separations Pd(II) was preferentially sorbed/exracted leaving the co- existing elements in the aqueous phase thus very high separation factors were achieved ($5.1 \times 10^4$–$5.4 \times 10^4$). All elements concentrations were determined in the aqueous phase using FAAS.

## 4. Conclusion

Pd(II) could be selectively separated and preconcentrated from different natural samples without interferences from common metal and precious metal ions in 10 mol/dm$^3$ $H_2SO_4$ by SE and 0.5 for SPE using PET in MIBK or PET immobilized on SG, respectively and spectrophotometrically determined. The two separation techniques were found accurate and precise without noticeable differences. PET and PET-SG in the two techniques can be effectively recycled using 0.5% thiourea in 0.2 mol/dm$^3$ HCl as eluent which is an advantage from the environmental point of view and economical cost of the procedure. However, the decision to make preference of one of them over the other is still related to the applied samples. If Pd(II) is present in highly acidic medium (other than HCl), it is recommended to use SE as it can withstand the drastic acid conditions whereas when dealing with mild acid concentration PET-SG can be preferably applied to gain higher preconcentration factor and to avoid the use of organic solvents.

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