NOVEL PALLADIUM(II) SELECTIVE MEMBRANE ELECTRODE BASED ON 4-[(5-MERCAPTO-1,3,4-THIADIAZOL-2-YLIMINO)-METHYL]BENZENE-1,3-DIOL

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A plasticized poly(vinyl chloride) membrane electrode based on 4-[(5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl]benzene-1,3-diol (**L**) for highly selective determination of palladium(II) (in $PdCl_4^{2-}$ form) is developed. The electrode showed a good Nernstian response (29.6 ± 0.4 mV per decade) over a wide concentration range (3.1×10^{-7} to 1.0×10^{-2} mol l^{-1}). The limit of detection was 1.5×10^{-7} mol l^{-1}. The electrode has a response time of about 20 s, and it can be used for at least 2 months without observing any considerable deviation from Nernstian response. The proposed electrode could be used in the pH range of 2.5–5.5. The practical utility of the electrode has been demonstrated by its use for the estimation of palladium content in aqueous samples.

Keywords: Palladium(II); Ion selective electrodes; PVC membrane; Potentiometry; 4-[(5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl]benzene-1,3-diol; Electrochemistry; Electroanalysis.

Palladium is a precious metal with an extensive use in different fields of science and technology such as metallurgy, chemical catalysis and medicine[1]. Especially, in recent years, the most important application of palladium, together with other platinum group metals (PGM) such as platinum and rhodium, has been connected with three-way catalytic converters for car engines to reduce the emission of carbon monoxide, hydrocarbons, and nitrogen oxides to the atmosphere[2]. Palladium is emitted in a particulate form together with a relatively high soluble fraction and may deposit to accumulate in vegetation and on the road surface and then enter the humans through breathing airborne particulate matter or by the food chain[3]. It is well known that palladium and its compounds are powerful sensitizing

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agents that may cause allergic reactions such as contact dermatitis, rhinitis, conjunctivitis, asthma, and urticaria[4]. Therefore, the detection of trace amounts of palladium in various matrices has attracted considerable interest in recent years[5,6].

Among the various analytical techniques, electrothermal atomic absorption spectrometry (ETAAS)[7,8], inductively coupled plasma atomic emission spectrometry (ICP-AES)[9], inductively coupled plasma mass spectrometry (ICPMS)[10–12] and adsorptive stripping voltammetry (ASV)[13] are the most widely used techniques for determination of palladium in a wide variety of biological and environmental samples. However, these methods are either time-consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. On the other hand, in recent two past decades, the application of carrier based ion-selective electrodes (ISEs) has become a well-established routine analytical technique for the determination of various cations and anions in different matrices[14–17]. The most important properties of these electrodes are the high-speed sample analysis, portability of the device, sample non-destructive, on-line monitoring, cost effectiveness and wide linear range[18–22].

Numerous studies have unambiguously established that sulfur-containing ligands are highly selective for Pd(II), classified as a "soft" Lewis acid[23–28]. In this paper we report on the fabrication of an ISE based on 4-[(5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl]benzene-1,3-diol (**L**) (Fig. 1) as a neutral and lipophilic ionophore for monitoring trace amounts of palladium in aqueous samples.

EXPERIMENTAL

Reagents and Apparatus

Reagent grade chemicals were used without any further purification. Stock solutions were prepared with doubly distilled water. Dibutyl phthalate (DBP), dioctyl phthalate (DOP), tris(2-ethylhexyl) phosphate (TEHP), dioctyl sebacate (DOS), tetrahydrofuran (THF), tetrabutylammonium perchlorate (TBAP), hexadecyltrimethylammonium bromide (HTAB), tetraoctylammonium perchlorate (TOAP), palladium dichloride ($PdCl_2$) and high relative

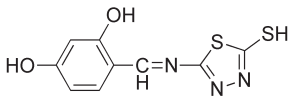

FIG. 1
Structure of 4-[(5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl]benzene-1,3-diol (**L**)

molecular weight poly(vinyl chloride) (PVC) were obtained from Merck or Sigma and used without any further purification. 2-Nitrophenyl octyl ether (NPOE) was purchased from Acros. The sodium salts of anions and all other chemicals were of the highest purity available from Merck, and they were used without further purification. The acetate buffer solution containing appropriate amount of 0.1 M acetic acid and 0.1 M sodium acetate was adjusted to pH 4.0 with sodium hydroxide solution and utilized to adjust pH of the test solution.

Absorbance spectra were recorded in nm using a Perkin–Elmer spectrophotometer (Lambda 25) equipped with a thermostated bath (Huber polystat cc1). For complexation studies, the temperature of the cell holder was maintained at 25 ± 0.1 °C.

Synthesis and Characterization of the Ionophore

The ligand **L** was synthesized as follows: 6.66 g of 5-amino-1,3,4-thiadiazole-2-thiol was weighted and transferred to a 250 ml flask containing 10 ml ethanol. An equimolar amount (6.91 g) of 2,4-dihydroxybenzaldehyde was added to this solution and heated at 100 °C under stirring. The resulting mixture was refluxed during 24 h. After complete dissolution of initial reagents, 10 µl of concentrated HCl (36.5% w/w, d = 1.18 g mol^{-1}) was added to the solution to start the reaction. Refluxing and stirring was continued for 8 h. The resulting yellow product was filtered and washed several times with ethanol. The product was then recrystallized from diethyl ether to give a purified sharp yellow powder. IR and ^{1}H NMR spectra confirmed the structure of the ligand. IR (KBr): 3309.2, 3139.3, 1635.2, 1520.7, 1318.9, 1173.5, 1064.8, 966.2, 688.7. ^{1}H NMR (DMSO): 14.35, 1 H (S-H); 11.35, 1 H (O-H ortho); 11.69, 1 H (O-H para); 8.65, 1 H (CH=N); 7.66, 6.43 and 6.34, 3 H (phenyl ring).

Preparation of the Electrode

The general procedure in order to prepare the PVC membrane was to mix thoroughly 1 mg of ionophore (**L**), 0.5 mg of additive (TOAP), 33.5 mg of powdered PVC and 65 mg of plasticizer NPOE in a glass dish of 2 cm diameter. The mixture was then completely dissolved in 5 ml of fresh THF. The solvent was slowly evaporated until an oily concentrated mixture was resulted. A Pyrex or Teflon tube (3–5 mm i.d. on the top) was dipped into the mixture for 10 s, so a membrane was formed. The tube was then pulled out from the mixture and kept at room temperature for 24 h. The tube was then filled with internal filling solution of 1.0×10^{-3} M $PdCl_2$ containing 0.2 M NaCl. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M solution of $PdCl_2$ containing 0.2 M NaCl.

EMF Measurements

A cell assembly of the following type was used: Ag | AgCl, KCl (3 M) | internal solution: 1.0×10^{-3} M $PdCl_2$, 0.2 M NaCl | PVC membrane | test solution | Hg | Hg_2Cl_2, KCl (sat.).

The EMF observations were made relative to a double-junction saturated calomel electrode with the chamber filled with an ammonium nitrate solution. A double-junction Ag|AgCl electrode (Metrohm) was used as the internal reference electrode.

RESULTS AND DISCUSSION

Distribution of Different Palladium Species in Aqueous Solution

The aqueous speciation of palladium has been comprehensively studied by some research groups[29–31]. It is well known that palladium forms chloro–aqua complexes in the form $PdCl_r(H_2O)_{4-r}^{2-r}$, where r can take a value between 0 and 4. The concentration ratios of the different aqua palladium species depend on the concentration of chloride ions present in the solution. It is reported that at high chloride concentrations, tetrachloropalladium ($PdCl_4^{2-}$) is the dominant species[31].

The influence of chloride ion concentration on the slope of the electrode is shown in Fig. 2. Obviously, the electrode does not show any Nernstian response at low chloride concentrations. This is probably due to the fact that at lower chloride concentrations a mixture of palladium species is present in the solution causing a mean response of the electrode. As chloride ion concentration increases, the slope of the electrode decreases and tends to level off at ca. 30 mV per decade. As mentioned above, at higher chloride concentrations the major species is $PdCl_4^{2-}$, which is probably responsible for the observed slope. Similar behavior has been previously reported in developing a Pt(II) ion-selective electrode[32]. Therefore, in all experiments the electrode potential was measured in the excess of chloride ion concentration ($[Cl^-] = 0.2$ mol l^{-1}).

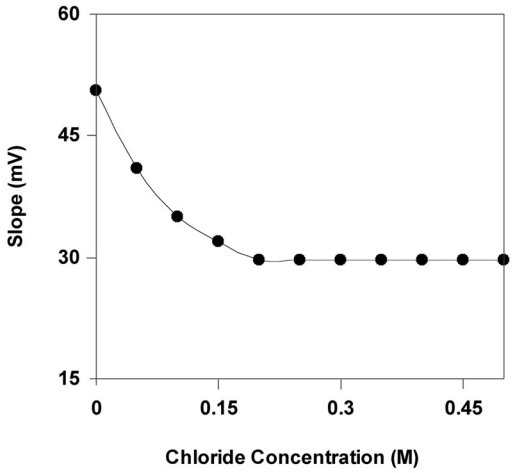

FIG. 2
Effect of excess chloride ion concentration on the slope of the electrode

Complex Formation

In order to determine the stoichiometry and stability of the resulting **L** complex with Pd(II) ion, the spectra of a series of solutions containing a constant concentration of ligand (5.0×10^{-5} mol l^{-1}) at 25 °C and varying amounts of the metal ion were obtained in acetonitrile and the results are shown in Fig. 3. As can be seen, the complexation was accompanied by decreasing in the absorption band of the **L** at 405 nm. The obtained molar ratio plot (absorbance versus [Pd(II)]/[**L**] at wavelength of 405 nm is shown

TABLE I
Formation constants of different metal–**L** complexes in acetonitrile

Metal	log K_f	Metal	log K_f
Pd(II)	6.82 ± 0.03	Hg(II)	5.35 ± 0.02
Cu(II)	5.27 ± 0.03	Ni(II)	4.12 ± 0.04
Zn(II)	4.77 ± 0.02	Co(II)	3.86 ± 0.02
Pt(II)	5.31 ± 0.03	Cr(III)	4.45 ± 0.02
Cd(II)	3.60 ± 0.01	Fe(III)	4.44 ± 0.05

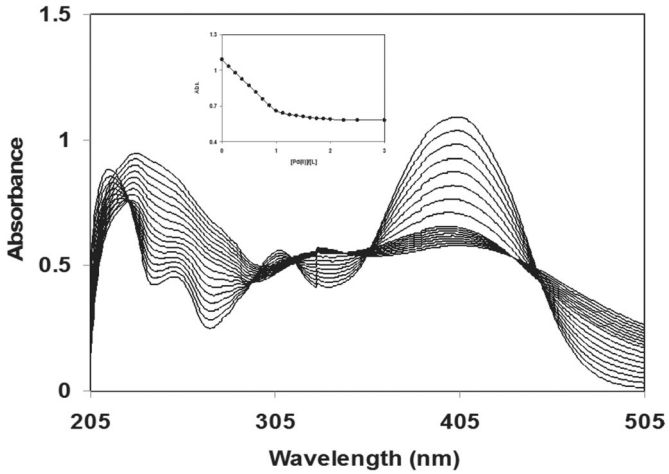

FIG. 3
UV-Vis absorption spectra of ligand (**L**) in acetonitrile (5.0×10^{-5} mol l^{-1}) in the presence of increasing concentration of Pd(II) ion. Corresponding molar ratio plot at 405 nm is shown in the inset

in the inset of Fig. 3. As can be seen, the absorbance–molar ratio plot revealed a level off at [Pd(II)]/[**L**] molar ratio of 1, emphasizing the formation of 1:1 (metal to ligand) complex in solution. Also, the complexation of **L** with a number of metal ions was investigated. The formation constants of the resulting 1:1 complexes are listed in Table I. As can be seen, the **L** with the most stable complex with Pd(II) ion is expected to act as a selective ionophore for preparation of Pd(II) ion-selective membrane electrodes. The formation constants of the resulting complex between cations and **L** were evaluated by SQUAD program[33,34].

Membrane Composition

It is well known that some important features of the PVC based membranes, such as the nature and amount of ionophore, the properties of the plasticizer, the plasticizer/PVC ratio and the nature of additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes[35–37]. A survey on the literature shows that the usual range of composition in the preparation of PVC matrix membrane electrodes is 1–7% ionophore, 28–33% PVC (internal matrix), 60–69% plasticizer (solvent) and 0.03–2% lipophilic anionic or cationic salts as membrane additives[38]. Therefore, the optimum membrane composition was sought for within this composition range. In addition, the contribution of the matrix (without ionophore) to the electrode response was studied. The results are summarized in Table II.

The nature of plasticizer improves the sensitivity and stability of PVC-based sensors. Plasticizers need to fulfill the four principal criteria: high lipophilicity, solubility in the polymeric membrane (no crystallization) as well as no exudation (one-phase system) and good selectivity behavior of the resulting membrane. The nature of plasticizer also influences the dielectric constant of the membrane phase[37] and, therefore, it is expected to play an important role in the performance of ISEs. In our work, five plasticizers of different polarity including DOP (ε_r = 5.0), DBP (ε_r = 6.42), DOS (ε_r = 4.0), TEHP (ε_r = 4.8) and NPOE (ε_r = 24.0) was used. As can be seen from Table II, NPOE gives the best response slope of the five plasticizers.

The lipophilic additives can significantly influence the performance characteristics of PVC-based ISEs not only via improving the response behavior and selectivity, but also by possible catalyzing the exchange kinetics at the sample solution–membrane interface[35]. The studies by Simon and coworkers[39] have shown that there is an optimal concentration of lipophilic salts in the membrane, which gives the highest sensitivity and selectivity. Thus,

TABLE II
Optimization of membrane ingredients

Membrane No.	Composition of membrane, wt.%				slope mV per decade	linear range mol l^{-1}
	PVC	plasticizer	additive	ionophore		
1	33.0	66 (DBP)	0.0	1.0	21.2 ± 0.5	8.4×10^{-6} to 1.0×10^{-2}
2	33.0	66 (TEHP)	0.0	1.0	19.3 ± 0.2	3.2×10^{-5} to 1.0×10^{-2}
3	33.0	66 (DOP)	0.0	1.0	20.6 ± 0.3	2.7×10^{-5} to 1.0×10^{-2}
4	33.0	66 (DOS)	0.0	1.0	15.5 ± 0.4	6.5×10^{-5} to 1.0×10^{-2}
5	33.0	66 (NPOE)	0.0	1.0	27.8 ± 0.4	1.0×10^{-6} to 1.0×10^{-2}
6	33.0	65 (NPOE)	1.0 (TBAP)	1.0	28.1 ± 0.5	8.3×10^{-7} to 1.0×10^{-2}
7	33.0	65 (NPOE)	1.0 (HTAP)	1.0	28.5 ± 0.4	9.1×10^{-7} to 1.0×10^{-2}
8	33.0	65 (NPOE)	1.0 (TOAP)	1.0	29.0 ± 0.3	4.6×10^{-7} to 1.0×10^{-2}
9	33.5	65 (NPOE)	0.5 (TOAP)	1.0	29.6 ± 0.4	3.1×10^{-7} to 1.0×10^{-2}
10	32.5	65 (NPOE)	1.5 (TOAP)	1.0	28.3 ± 0.4	6.4×10^{-7} to 1.0×10^{-2}
11	33.0	65 (NPOE)	0.5 (TOAP)	1.5	28.1 ± 0.3	5.9×10^{-7} to 1.0×10^{-2}
12	34.0	65 (NPOE)	0.5 (TOAP)	0.5	27.7 ± 0.3	8.7×10^{-7} to 1.0×10^{-2}
13	33.5	65 (NPOE)	0.5 (TOAP)	0.0	6.6 ± 0.4	4.8×10^{-4} to 1.0×10^{-2}

addition of a little amount of additives may improve the response characteristics of the proposed electrode. From the data presented in Table II, it is obvious that the addition of TOAP increases the sensitivity of the electrode response considerably. The use of 0.5% TOAP significantly improves the performance characteristics of the membrane electrode and results in a Nernstian behavior of the electrode (No. 9). Thus, the membrane No. 9 obtained with the PVC/NPOE/**L**/TOAP ratio of 33.5:65:1.0:0.5 shows a Nernstian slope of 29.6 mV per decade over very wide Pd(II) concentration range.

pH Effect

The effect of pH of the test solution (1.0×10^{-3} M Pd(II)) on the potential response of the electrode was investigated over the pH range 1–7, where pH was adjusted with dilute HNO_3 or NaOH solutions. As illustrated in Fig. 4, within the pH range 2.5–5.5, the potential did not vary by more than ±1.0 mV. At lower pH values, protonation of the ligand is possible, which can result in the loss of its complexing ability with palladium ions, then the membrane sensor responds to hydrogen ions, while the observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Pd(II) ion in solution. Thus, the above range may be taken as the working pH range of the proposed sensor.

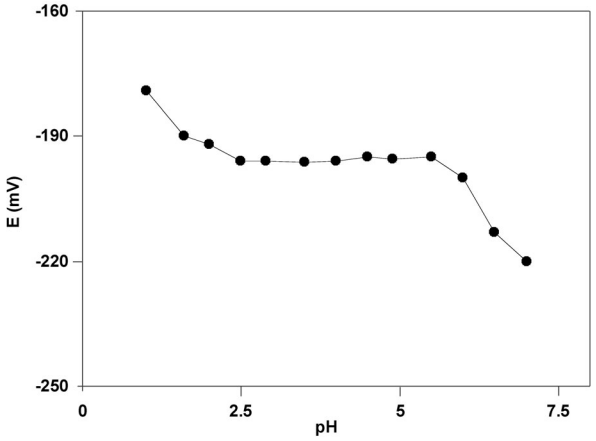

FIG. 4
Effect of pH on the response of the palladium ISE

Response Time, Calibration Curve and Lifetime

The response time is an important factor for any ISE. The average time required for palladium ISE to reach a potential within ±0.5 mV of the final equilibrium value after successive immersion in a series of Pd(II) solutions, each having a 10-fold difference in concentration from 1.0×10^{-6} to 1.0×10^{-2} mol l^{-1}, was considered. The results are given in Fig. 5. As can be seen, in the whole concentration range, the static response times of the membrane electrode were obtained in a short time (about 20 s). The PVC membrane electrode prepared, filled by conventional inner filling solution and operated under optimal experimental conditions shows a linear response to the concentration of palladium ion in the range 3.1×10^{-7} to 1.0×10^{-2} mol l^{-1}, with a Nernstian slope of 29.6 mV per decade of palladium ion concentration (Fig. 6). The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 1.5×10^{-7} mol l^{-1}. For the investigation of the stability and the lifetime of the Pd(II) membrane sensor, five sensors were tested over a period of 2 months. During this period, the electrodes were in daily use over an extended period of time (1 h per day). Their slopes and linear ranges were measured. The results are summarized in Table III, where it is concluded that, after 2 months, slight changes were observed in the slopes and linear ranges. This prominent feature rises from the optimum lipophilicity of the ionophore and plasticizer, which ensures stable potentials and long lifetime[40–42].

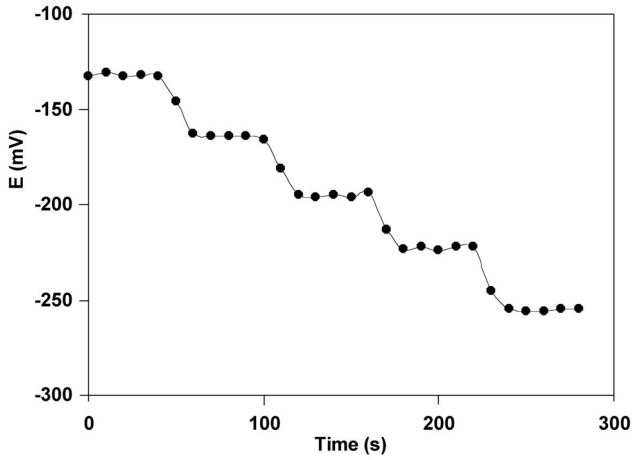

FIG. 5
Dynamic response time of the Pd(II)-membrane sensor over a 1.0×10^{-6} to 1.0×10^{-2} M solution

Potentiometric Selectivity

The potentiometric selectivity of the optimized electrode for palladium ion against other interfering ions was determined by separated solution method (SSM)[43]. According to SSM, the potential difference ($E_j - E_i$) was measured with each of two separate solutions of interfering and palladium ion, respectively. Assume that solutions of the primary ion and interfering ions are at the same level of activity $a_i = a_j = 1.0 \times 10^{-3}$. Then, the selectivity coefficient was calculated by using the following equation:

TABLE III
The lifetime behavior of the Pd(II)-membrane sensor (n = 3)

Linear range, mol l^{-1}	Slope	Day
3.1×10^{-7} to 1.0×10^{-2}	29.6 ± 0.4	1
3.8×10^{-7} to 1.0×10^{-2}	29.1 ± 0.6	10
4.4×10^{-7} to 8.8×10^{-3}	28.8 ± 0.5	20
5.3×10^{-7} to 5.6×10^{-3}	28.3 ± 0.4	30
6.6×10^{-7} to 3.1×10^{-3}	27.9 ± 0.9	40
7.5×10^{-7} to 2.5×10^{-3}	27.7 ± 0.9	50
8.9×10^{-7} to 1.2×10^{-3}	27.2 ± 0.8	60

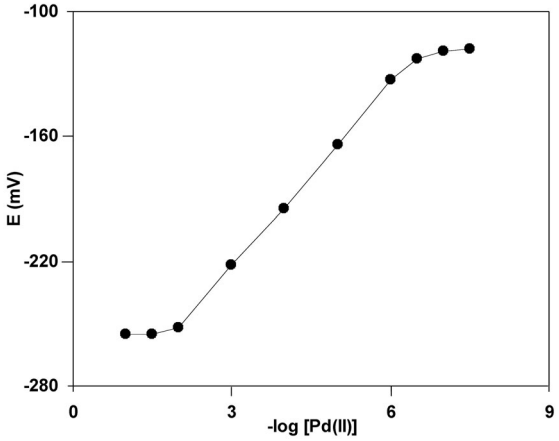

FIG. 6
Calibration graph for platinum ISE based on **L** (composition No. 9)

$$\log K = \frac{E_j - E_i}{S} - \log a_j^{Z_i/Z_j} + \log a_i \qquad (1)$$

where E_j and E_i are the measured EMFs for the solution of interfering and palladium ions, S is the calibration slope of the sensor, Z_i and Z_j are the charges of palladium and interfering ions, and a_i and a_j are the activities of palladium and interfering ions. The resulting selectivity coefficients are summarized in Table IV. As can be seen for all ions used, they would not disturb the functioning of the Pd(II) ion-selective membrane. Hence, these cations are not expected to interfere with the functioning of the proposed Pd(II) selective sensor even at high concentration levels.

TABLE IV
Selectivity coefficient of various interfering ions (n = 3)

Interfering ion	–log K	Interfering ion	–log K
Cd(II)	3.18 ± 0.35	Al(III)	3.78 ± 0.28
Zn(II)	3.37 ± 0.33	Mn(II)	3.69 ± 0.27
Pb(II)	3.24 ± 0.32	Co(II)	3.15 ± 0.33
Ni(II)	3.01 ± 0.39	Cr(III)	3.21 ± 0.34
Pt(II)	2.08 ± 0.33	Ba(II)	6.10 ± 0.31
Hg(II)	2.39 ± 0.38	Ca(II)	5.97 ± 0.25
Cu(II)	2.24 ± 0.37	K(I)	5.37 ± 0.25
Fe(III)	3.23 ± 0.30	Na(I)	6.81 ± 0.26

Analytical Application

The electrode was applied to the direct determination of palladium in spiked waste water samples and the results are shown in Table V. As can be seen, the recovery of palladium is almost quantitative. Then, the proposed sensor was found to work well under laboratory conditions. It is clear that the amount of Pd(II) ions can be accurately determined using the proposed sensor.

In summary, the proposed Pd(II) ion-selective membrane electrode, exhibits a Nernstian response over a wide concentration range, good reproducibility, fast response time and fairly good selectivity for Pd(II) over other potentially interfering ions. The preparation of the electrode is easy and

not expensive. The electrode is mechanically and chemically stable over a period of 2 months. The good selectivity and fast response may enable its use in routine analysis of palladium in real samples.

TABLE V
Determination of the Pd(II) in spiked waste water samples (n = 6)

Sample No.	Added, ppb	Found, ppb	RSD, %	Recovery, %
1	106	111.5 ± 5.7	5.1	105.2
2	266	256.4 ± 12.3	4.8	96.4
3	532	505.9 ± 23.2	4.6	95.1

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