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Short communication

SHORT COMMUNICATION

A novel optode sensor for the determination of palladium(II) in water and a hydrogenation catalyst

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Abstract: A novel optical sensor was established to determine palladium(II) based on the immobilization of 1-(2-pyridylazo)-2-naphthol (PAN) on a triacetylcellulose membrane. Palladium ions react with the immobilized PAN and cause a decrease in the absorbance of the membrane at 469 nm. The response time of the optode was 8–10 min depending on the concentration of Pd(II) ions. This sensing phase had a dynamic linear range of 0.10–12.0 μg $\mathrm{ml^{-1}}$ palladium ions with a limit of detection of 65 ng $\mathrm{ml^{-1}}$. The sensor can readily be regenerated using an ethylenediamine solution. The sensor could be fully regenerated, and the color change was fully reversible. The method was successfully applied for the determination of Pd(II) in synthetic aqueous solutions and in a hydrogenation catalyst sample.

Keywords: optode; 1-(2-pyridylazo)-2-naphthol (PAN); palladium(II); hydrogenation catalyst; triacetylcelluose.

INTRODUCTION

The significance of palladium as a transition metal lies in its wide spectrum of application, especially in the electrical and electronic industries, catalyst, dentistry and medical devices, jewelry and recently as nano-particles for the development of new active catalyst.[1–3] It was thus considered worthwhile to explore the possibilities of developing a simple, sensitive and selective method for the determination of traces of palladium in various samples. Many methods have already been developed for the determination of palladium in real samples. These are based on atomic absorption spectrometry (AAS) and extractive spectrophotometric methods.

The AAS instrumental techniques are: atomic absorption (AAS), both flame (FAAS) and electrothermal spectrometry (GFAAS).[4] Although these methods

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have good sensitivity, they require expensive instruments, well-controlled experimental conditions and a profound sample preparation.

The extractive spectrophotometric methods employ many organic complexing reagents[5,6] which can be used for the determination of palladium, but they suffer from several disadvantages, such as low sensitivity, incomplete extraction and interference from a large number of foreign ions.[7–9]

In this communication, the first optode for the determination of palladium ions is introduced. Although a few sensors exist for the determination of palladium,[10–11] there are some difficulties, such as pretreatment, higher detection limits and complex procedures. In the present study, PAN was employed as an ionophore because of its ability to form highly colored complexes with transition metals[12] and its solubility in the membrane phase. It was immobilized on a triacetylcelluose membrane for the determination of low levels of palladium ions. The membrane responds to palladium ions by changing in absorbance, it can be applied as a relatively selective reagent for Pd(II) at pH 2.0.

EXPERIMENTAL

Reagents

All the reagents such as PAN and ethylenediamine were supplied by Merck and all solutions were prepared with double distilled water. The Pd(II) solution was prepared by dissolving 1.664 g of palladium chloride (Merck) in a minimum amount of 2.0 mol L^{-1} hydrochloric acid solution in a one liter volumetric flask and finally made up to the mark with an identical hydrochloric acid solution. It was standardized by an indirect method using EDTA.[13]

Apparatus and measurement procedure

A Shimadzu 1601 PC UV–visible spectrophotometer with 1.0 cm quartz cells was used for the absorbance studies. A Jenway model 3510 pH-meter with a combined glass electrode was used for pH adjustment. A Sense AA GBC Scientific Equipment atomic absorption spectrometer was used to compare the result.

The membrane prepared according to a procedure given in the literature[18] was placed in a 2.5 ml trichloroacetic acid buffer (0.20 M) of pH 2.0 for several seconds to reach equilibrium. The membrane was placed vertically inside a quartz cell, hence, the optical path passed straight through the membrane. Then a solution with a specific concentration of analyte was added and the difference in the absorbance of the immobilized form of PAN was measured at 469 nm before and 600 s (equilibration time) after the addition of the analyte. In addition, no difference in the absorbance at 469 nm of the membrane was detected in a blank solution during 600 s.

RESULTS AND DISCUSSION

The absorption spectra of immobilized PAN obtained after equilibration in buffer solutions (pH 2.0) containing different concentrations of palladium are shown in Fig. 1. The spectral change is because of the addition of Pd(II) ions and the complex formation. Considering Fig. 1, the Pd(II) complex has two absorption peaks at pH 2.0, the first one of which is located on 659 nm and the second at 611 nm. Also, it can be seen that upon addition of increasing amounts of Pd(II) ions, the absorbance of the complex increases at the expense of the absorbance of free ligand at 469 nm, showing a sharp isosbestic point at 515 nm, supporting the formation of a 1:1 metal ion–PAN complex. The wavelength of 469 nm was selected for further studies because of the higher sensitivity at this wavelength.

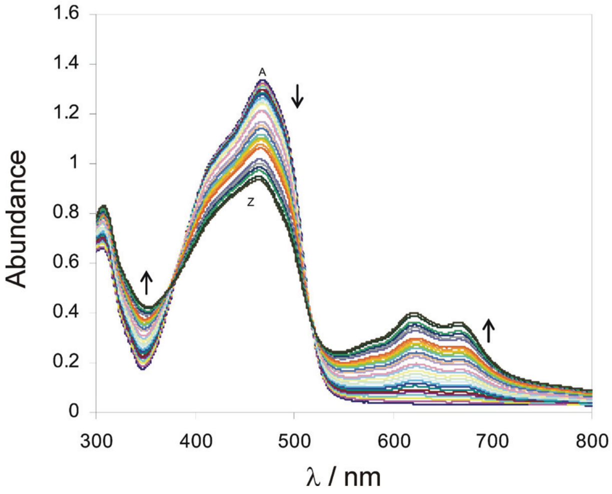

Fig. 1. Absorption spectra of the optode film in response to the addition of Pd(II) ions in the concentration range 0–14.0 μg mL^{-1} at pH 2.0 (A–Z show the increase in concentration of Pd(II) ions by the addition of 0.46 μg ml^{-1} Pd(II) ions in each interval).

The absorbance was measured at 469 nm for 1.0×10^{-5} M (2.0 μg ml^{-1}) palladium ions at different pH values. The blank membrane (membrane without PAN in the buffer solution) was taken as the reference. The absorbance measurement are expressed as absorbance difference, which was defined as the difference between the absorbance of the immobilized PAN alone and the absorbance of the Pd(II)–PAN complex at 469 nm. With increasing pH value from 1.0 to 5.0, the difference in the absorbance reached a maximum at pH 2.0 and then decreased sharply. This phenomenon might be due to the fact that at low pH values (pH < 2), complexation is weak. At pH values higher than 2, Pd(II) forms different hydroxide species ($\mathrm{Pd(OH)}_n^{(n-2)-}$), which make complex formation with PAN impossible.[26]

The absorbance difference *versus* the Pd(II) concentration exhibits a linear range between 0.10 and 12.0 μg ml^{-1}. The regression equation is:

$$R = 0.0241c + 0.0251 \tag{1}$$

where R is the response expressed as the decrease of the absorbance of the film at 469 nm for a fixed time of 10 min and c is the concentration of Pd(II) in μg ml^{-1}, with a correlation coefficient of 0.9987. The detection limit, which was estimated as the concentration of analyte producing an analytical signal equal to three times the standard deviation of the blank signal, was found to be 65 ng ml^{-1}.

An important analytical feature of any optode film is its response time. In this work, the optode film was found to reach 95 % of the final signal after 8–10 min, depending on the concentration of Pd(II) ions. In general, the response time was lower in concentrated solutions than in dilute ones.

The lifetime of membrane was determined by adding a buffer solution (pH 2.0) in a quartz cell including a film. The signal was recorded at wavelength of 469 nm over a period of about 24 h. No significant loss of the indicator occurred during this time. When the membrane was exposed to light, no drift in the signal was observed and the membrane was stable over the period of the experiment with no leaching of the indicator.

Concerning membrane regeneration, the best result was obtained by applying ethylenediamine, which gave short membrane regeneration times (3–5 s). After regeneration before the next palladium concentration measurement, the optode should be placed in buffer (pH 2.0) for 15 min.

To determine the selectivity of the proposed method, interference of a number of ions was studied. The main interference was Cu(II), which can be eliminated by 0.10 M ascorbic acid. It is apparent from the study that discrimination between different metals can be achieved by the control of several parameters, including the absorption wavelength, the pH and the sample contact time in addition to the use of masking agents.

The developed optical sensing method for Pd(II) was successfully applied for the determination in synthetic aqueous solutions and hydrogenation catalyst. Various water samples with different contents of Pd(II) and a hydrogenation catalyst were prepared and analyzed employing the recommended procedure. The results were in perfect agreement with those obtained by direct atomic-absorption spectrometry. The results are presented in Table I.

TABLE I. Determination of Pd(II) in synthetic aqueous solutions and a hydrogenation catalyst by the proposed optode method and by AAS

Sample	Palladium claimed, wt. %	Pd (II) added, μg ml^{-1}	Pd (II) found, μg ml^{-1}		Recovery %
			AAS Method	Proposed method	
Solution 1	–	1.50	1.48	1.46	97.3
Solution 2	–	3.40	3.37	3.33	97.9
Solution 3	–	5.50	5.52	5.46	99.3
Solution 4	–	8.80	8.80	8.75	99.4
Solution 5	–	11.40	11.42	11.45	100.4
Catalyst	0.03–0.04[a]	–	0.037[b]	0.035[b]	–

[a] The catalyst 7741-T, which is used in the Amir Kabir Petrochemical Co., Iran, was treated twice with 10 ml portions of aqua regia; [b] the unit is wt. %

CONCLUSIONS

The described optode is easily prepared and provides a simple and inexpensive means for the determination of Pd(II) ions. The membrane responds to palladium ion by decreasing absorbance of PAN. The sensor can be regenerated readily with a solution of ethylenediamine and has a long lifetime. The response of the optode was reproducible and the optode presented a good selectivity for Pd(II) over other metal ions, except for Cu(II) which can be masked using ascorbic acid. Since the sensor does not require solvent extraction, it can compete with standard optical fibers. The sensor can be applied for the analysis of real samples.

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ИЗВОД

НОВИ ОПТИЧКИ СЕНЗОР ЗА ОДРЕЂИВАЊЕ ПАЛАДИЈУМ(II) ЈОНА У ВОДИ И У КАТАЛИЗАТОРУ ЗА ХИДРОГЕНОВАЊЕ

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Формиран је нови оптички сензор за одређивање паладијум(II) јона заснован на имобилизацији 1-(2-пиридилазо)-2-нафтола (ПАН) на мембрани од триацетилцелулозе. Јони паладијума реагују са имобилисаним ПАН-ом и проузрокују смањење абсорбанције мембране на 469 nm. Време одзива сензора је 8–10 min, зависно од концентрације Pd(II) јона. Ова сензорска фаза поседује динамички линеарни одзив у опсегу концентрација Pd(II) јона од 0,10––12,0 µg ml^{-1}, са границом детекције од 65 ng ml^{-1}. Сензор се лако регенерише раствором етилендиамина. Он се потпуно регенерише, а промена боје је потпуно повратна. Метод је успешно примењен за одређивање Pd(II) у синтетичким воденим растворима и у катализатору за хидрогеновање.

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