Dipyridyl-functionalized Nanopore Sized Silica Gelsas New Efficient Electrode Modifiers in Carbon Paste Electrodes

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ABSTRACT

The surface of activated nanopore sized silica samples was chemically modified by covalent grafting of amine groups, by reaction with N-(2-aminoethyl)-3-aminopropyl-trimethoxy silane. Nanopore sized dipyridyl-functionalized silica gels have been prepared by refluxing grafted amino nanopore sized silica gel with 2,2'-dipyridyl ketone in toluene under the argon atmosphere. The incorporation of nanopore sized organofunctionalized silica gel (DPNSG) particles within carbon paste leads to improved potentiometric detection of copper (II) in acetate medium. The enhanced sensitivity was attributed to selective interaction of copper (II) by the approved surface dipyridyl groups of silica gel. The modified electrode presented high performance, high sensitivity in wide cation activity ranges and good long term stability. The method was satisfactory and was used to determine the copper ion concentration in waste waters, contaminated by this metal.

KEYWORDS

Modifier, Carbon Paste Electrode; Nanopore; Silica gel; Copper; Lifetime; Potentiometric.

1. INTRODUCTION

The introduction of a chemical modifier, able to preconcentrate metallic ions on the electrode surface either by complexation or electrostatic attraction, can lead to more sensitive electroanalytical procedures with lower detection limit values. Silica-based organic–inorganic hybrids are attractive composite materials. They combine in a single solid both the properties of a rigid three-dimensional silica network with the particular chemical reactivity of the organic component(s). In particular, the design of nanopore sized silica-based adsorbents for the determination of toxic heavy-metal ions in aqueous solutions is a subject that has been intensively investigated [1]. For this purpose, a variety of organic functional groups can be grafted or incorporated onto the surface of the nanostructured channels, using ligand-functionalized organosilanes. Perhaps the greatest interest in these materials arises from the fact that most of them can be manufactured quite easily at room temperature by sol-gel processing. This processing involves the hydrolysis and condensation of silicon alkoxide precursors and the ability to immobilize enzymes within the silica network. They can maintain their biological activity and they can produce robust ceramic-carbon composites, using a silicate backbone as the solid binder. This led to several analytical applications, including ion determinations by direct potentiometry or ion-sensitive field-effect transistors (ISFETs) or electrolyte insulator semiconductor structure (EIS). A recent report describes the sensitive detection of heavy metal ions (Cd^{2+}, Pb^{2+}) using cyclodextrin-polysiloxane gel membranes [2]. A similar approach, with nonactin being the ionophore, resulted in an ammonium-sensitive ISFET [3]. A neutral carrier (dibenzo-18-crown-6), incorporated into the PVC membrane, deposited on a ferrocene-linked sol-gel glass and coated on a platinum electrode, was applied as a solid-state potentiometric sensor for potassium ions [4]. The resulting device

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displayed better performance than those obtained with the employment of plasticized PVC matrix membranes, having been impregnated with the same ionophore. A simple way to confine electronically insulating materials on an electrode surface, and to further exploit their properties in electrochemistry, was achieved by dispersing them into a conductive carbon-based composite, like carbon paste. Despite the ease of preparation and the good electrochemical properties, the main interest of carbon paste in the construction of modified electrodes is probably linked to the fact that this approach allows the usage of all types of silica-based materials. Carbon paste electrode (CPE) is one of the convenient conductive matrices to prepare the chemically modified electrodes (CMEs) by simple mixing graphite/binder paste and modifier. These kinds of electrodes are inexpensive and possess many advantages such as low background current, easy fabrication and rapid renewal [5].

In the recent years, we have successfully used nanoporous silica gel as well as some macrocyclic ligands as suitable ionophores or modifiers for the design of potentiometric sensors for heavy metals, such as Ag^{+} [6], Hg^{2+} [7], Ni^{2+} [8] and Cu^{2+} ions [9]. This paper describes the construction of a selective carbon paste electrode, modified with silica-based organic-inorganic hybrid materials. These materials contained dipyridyl groups covalently attached to the solid framework via a aminopropyl chain. The sensor properties were evaluated by its application to the determination of copper ions in waste water samples. The presence of rigid heterocyclic molecules such as pyridine, carrying hard N-donor atoms, as part of a macrocyclic ligand, has shown to have a marked influence on the coordination geometry at the metal centre [10]. The organofunctionalized nanopore sized silica, with groups containing S, N or O atoms, are very efficient materials to improve the lifetime of the proposed modified carbon paste electrode.

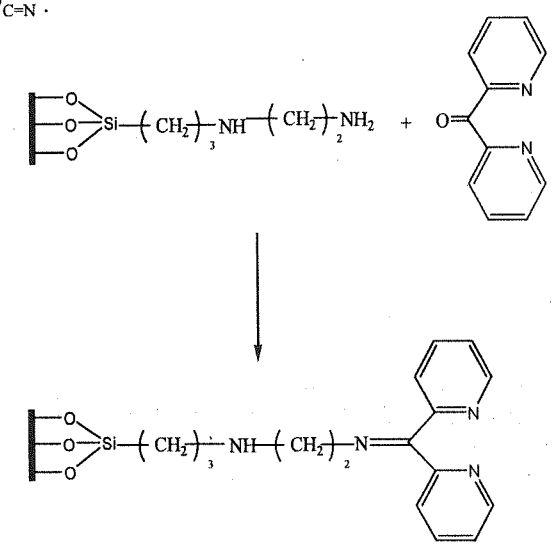
2. EXPERIMENTAL

A. Reagents

Silica gel 60 with a specific surface area of 500 m^2/g, hydrochloric acid, 3-(triethoxysilyl)- propylamine and the nitrate salts of the used cations were purchased from the Merck company. 2,2'-dipyridyl ketone 99% was purchased from Aldrich. The graphite powder with a 1-2 μm particle size (Merck) along with the paraffin oil (Aldrich) were of high purity and were used for the preparation of the carbon pastes. All of the working solutions were buffered at pH 5.5 ± 0.1, using a 0.05 M acetate buffer solution. The stock solutions of all cations (0.10 M) were prepared from the corresponding analytical grade salts and were diluted to the desired concentration by repeated dilution.

B. Functionalization of the Nanopore sized Silica Gel

Silica gel is an amorphous inorganic polymer having siloxane groups (Si-O-Si) in the bulk and silanol groups (Si-OH) on its surface. The latter are responsible for the chemical modifications that may occur on the silica surface. Because the commercial silica gel possesses a low concentration of surface silanol groups suitable for modification, the activation of silica gel surfaces is necessary. Because the commercial silica gel possesses a low concentration of surface silanol groups suitable for modification, activation of silica gel surfaces is necessary. For the preparation of the surface bound dipyridyl silica gel ligand (scheme 1), a nanopore sized silica gel was activated by refluxing in hydrochloric acid (4 M) for 24 h, where it was then washed with distilled water and dried completely. A mixture of 10 g of activated silica gel with 2 mmol of N-(2-aminoethyl)-3-aminopropyl-trimethoxy silane was refluxed in dry toluene for 24 h under an atmosphere of argon. The attained solid, grafted amino nanopore sized silica gel (GANSG), was washed with warm toluene three times and then was allowed to react with 2.5 mmol of 2,2'-dipyridyl ketone (DK) in refluxing toluene under the argon atmosphere. To remove the unreacted ketone, the solid was filtered and washed with warm ethanol and, afterwards, the excess of solvent was removed under reduced pressure in vacuum line at 30 °C for 3 h. The infrared spectrum of modified silica showed a band at 1632 cm^{-1} (Figure 1), which is characteristic of $\nu_{C=N}$.



SCHEME 1

Table 1 shows the elemental analysis for carbon and nitrogen for the GANSG and DPNSG. The quantity of molecules attached to nanoporous silica (after drying under vacuum) was calculated from the percentage of nitrogen in GANSG. The C/N molar ratio of GANSG, calculated from the elemental analysis is 5/2 and indicates a 3:1 stoichiometry between the silanol group (Si-OH) and the ligand. In addition, the results indicated that the

functionalization degree (L_0) is 0.15mmol/g. After reaction with (DK), the elemental analysis shows that about 90% of GANSG react with DK. The TGA of DPNSG (Figure 2) shows two decomposition states: one starting at 25°C (1.8% weight loss), assigned to water loss, and another mass loss between 140°C and 580°C (5.8% weight loss), assigned to the decomposition of organic pendant groups anchored onto silica gel and the water loss during the condensation of silanol to siloxane groups.

TABLE 1
THE ELEMENTAL ANALYSIS OF THE FUNCTIONALIZED SILICA GEL.

Functionalized Silica Gels	%C	%N
GANSG	0.91	0.42
DPNSG	2.74	1.73

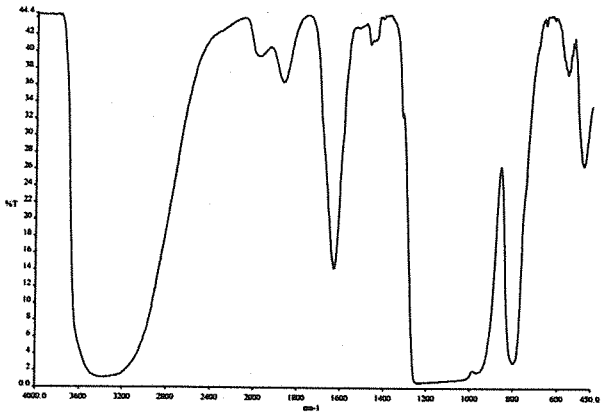


Figure 1: The infrared spectrum of Dipyridyl-functionalized silica gel.

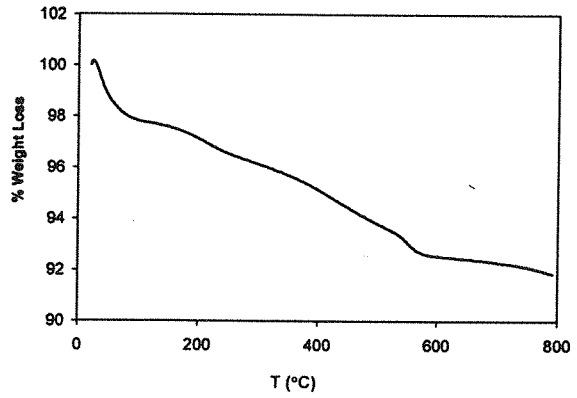


Figure 2: The thermogravimetric curve of Dipyridyl-functionalized silica.

C. Preparation of the Chemically Modified Carbon Paste Electrodes

The chemically modified carbon paste electrodes were prepared by thorough mixing graphite powder, 25% (w/w) paraffin oil and modifier in proportions of 10.3, 15.0 and 19.6% (w/w), respectively. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste.

D. Electrode Conditioning

Fresh modified electrode surfaces were conditioned by exposure to 1.0×10^{-4} M $Cu(NO_3)_2$ and 1.0×10^{-3} M $NaNO_3$ solution at pH 5.5, adjusted with a 0.01 M acetate buffer for 12 h. The electrodes were, then, rinsed with de-ionized water for 30 s.

E. Emf Measurements

All potentials were measured on a Corning model 125 pH/mV meter *vs* SCE. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. The electrochemical cell can be represented as follows:

Hg, Hg_2Cl_2(s), KCl (3 M) || sample solution | carbon paste electrode

Calibration graphs were constructed by plotting the potential, E, *versus* the logarithm of the copper ion concentration at constant pH, 5.5.

3. RESULTS AND DISCUSSION

A. General consideration

Carbon paste electrodes are typically investigated under zero-current conditions in a galvanic cell. The electromotive force (emf) across this cell is the sum of all individual potential contributions. Many of these are sample-independent, and the measured emf can usually be described *as* [11]:

$E_{CPE} = E_{matrix} + \Sigma E_J + \Delta E$

where E_{matrix} is the constant potential due to matrix resistance, ΣE_J is the summation of the liquid junction potentials at the sample/bridge electrolyte interfaces, which can be kept reasonably small and constant under well-defined conditions, and ΔE is the potential difference between the internal and external surface of the modified electrode. In the present case, however, we will only focus on the ΔE of the electrode, which can be divided into two separate potential contributions: a) the phase boundary potentials at the interface, b) the diffusion potential within the ion-selective electrode. While the potential at the CPE/test solution interface is dependent on the sample, the diffusion potential may become significant, if considerable concentration gradients of ions with different mobilities arise in the CPE surface. When the electrode is conditioned in the target ion solution, however, the diffusion potential is negligible in most cases of practical relevance. We, therefore, postulate:

$\Delta E = E_{Diffusion} + E_{PB} = E_{const} + E_{PB}$

where E_{PB} is the phase boundary potential at the CPE-sample interface, which is ideally a function of the sample ion activity according to the well-known Nernst equation:

$$E_{CPE} = E'_{const} + \frac{RT}{zF} \ln a_{Cu}$$

where z is the valency and a_{Cu} the activity of the uncomplexed Cu^{2+} ion, and R, T and F are the universal gas constant, the absolute temperature and the Faraday constant. It is now assumed that the interfacial ion transfer and complexation processes are relatively fast and, consequently, equilibrium is held at the interface.

B. Response Characteristics of the CPEs and Electrode Composition

The nanopore sized silica use in the heavy metal determination has been the subject of extensive research recently. This work, to the best of our knowledge, is the first attempt to apply modified silica gel for the selective copper ion determination in the presence of other metal ions.

In preliminary experiments, we found that the carbon paste electrodes, containing dipyridyl-nanopore sized silica, generated stable potentials in the solutions with copper ions, after a conditioning in a 1.0×10^{-4} M $Cu(NO_3)_2$ and 1.0×10^{-3} M $NaNO_3$ solution. The membranes revealed remarkable selectivity for Cu^{2+} relative to more common metal ions. This is likely due to the high selectivity of the functionalized silica gel for copper ion over other metal ions as well as the rapid exchange kinetics of the resulting complex. The presence of both nitrogen atoms as the soft coordination sites as well as the rigid heterocyclic dipyridyl molecule together with a more or less convenient cavity size seems to generate great affinity of ionophore toward Cu^{2+} ion.

The potentiometric responses shows that the electrode does not exhibit any sensibility to K^+ ,Na^+ ,Cd^{2+} ,Ni^{2+} ,Pb^{2+} ,Mg^{2+} ,Ca^{2+} ,Ba^{2+} concentration changes in the solution. Thus, it can be concluded that the changes in the membrane potential are induced by host-/guest complexation, which implies molecular recognition effects at the interface of the modified electrode and the aqueous solution [12].

The effect of membrane composition on the potentiometric response of the electrodes was investigated by varying the proportions of the ion carrier (DPNSG) and graphite powder. Table 1 presents the compositions of several typical electrodes, along with their response characteristics. The potential response of all the CPEs studied in the concentration range 1.0×10^{-8} to 1.0×10^{-1} M Cu^{2+} ion.

Based on the IUPAC recommendations [13], the critical response characteristics of the proposed electrode were assessed. Table 1 shows the slops, linear ranges and LODs of the resulting potentiometric calibration curves for the Cu^{2+} ion-selective electrodes, which obtained in buffered solutions at pH 5.5. As can be seen, an increase in the level of DPNSG in the CPE causes an increase of the slope of the calibration curve (compare CPE2 and CPE3).

As it seen from Table 2, the DPNSG-modified electrode obtained under optimal membrane ingredients with the graphite powder/paraffin oil/DPNSG percentage ratio of 60%/25%/15% shows a Nernstian slope of 28.4 mV/decade in a wide range of copper concentrations between 1.0×10^{-7} and 1.0×10^{-2} M Cu^{2+} ion (Figure 3). According to these results a carbon paste composition of CPE3 was used in further studies. The carbon paste electrode without modifer (CPE1), shows a nonlinear potentiometric response and as can be seen in Table 2, the slop is very low (~6.9 mV $decade^{-1}$).

The LOD, defined as the concentration of copper ion obtained when the linear regions of the calibration graphs are extrapolated to the baseline potentials. From Table 2, 8.0×10^{-8} M is obtained for the detection limit of the CPE5 that is at least one to two orders below than conventional polymeric membrane electrodes. We can now be considered competitive methods for the determination of free ion levels because the detection limits have been successfully reduced.

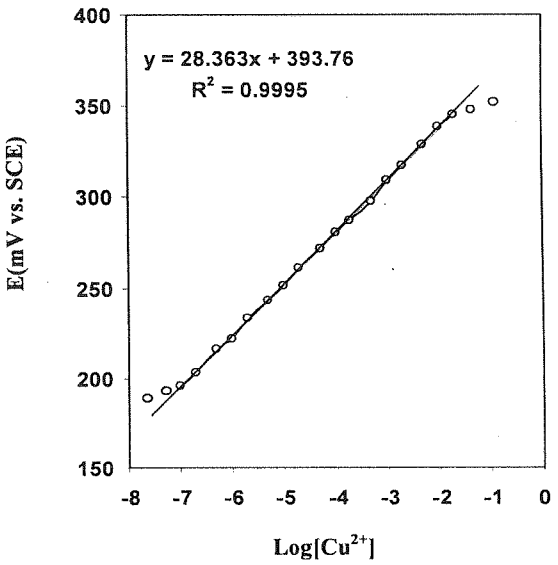


Figure 3: The calibration curve for the CPE3.

TABLE 2
COMPOSITION OF THE CARBON PASTE ELECTRODES AND THEIR POTENTIOMETIC RESPONSE CHARACTERISTICS OF CHEMICALLY MODIFIED ELECTRODES .

Electrode	Composition%			Slope (mV decade^{-1})	Linear range(M)	LOD(M)
	DPNSG	Graphite Powder	Paraffin Oil			
CPE1	0	75.0	25.0	~6.9(±2.2)	-	5.0×10^{-6}
CPE2	10.3	64.4	25.3	27.9(±1.0)	5.0×10^{-7} to 5.0×10^{-2}	3.0×10^{-7}
CPE3	15.0	60.0	25.0	28.4(±1.0)	1.0×10^{-7} to 5.0×10^{-2}	8.0×10^{-8}
CPE4	19.6	55.2	25.2	27.8(±1.2)	1.0×10^{-7} to 1.0×10^{-2}	8.0×10^{-8}

This was accomplished by effectively reducing zero current ion fluxes from the membrane interior, inner electrolyte solution, or both, which otherwise give rise to elevated local concentration levels at the membrane surface and therefore higher detection limits. Note that ion-selective electrodes with an inner aqueous electrolyte contact will invariably show a kinetic bias, even with very high membrane selectivities, and observed detection limits are typically still much higher than their thermodynamically predicted ones. Electrodes with a solid inner contact are promising alternatives in this regard, and their detection limits have so far remained in the nanomolar range.

C. Cleaning solution

For multiple successive analyses under various experimental conditions, the washing step with 0.05 M EDTA solution (pH 7) was required for the electrode to return to the starting potential. Similar to most electrochemical devices, based on the CMEs, regeneration procedures could be used, too. A fresh surface DPNSG-modified electrode could be produced by scraping out the old surface.

D. Response Time

The rate, at which reagents enter and leave the silica host matrix, is critically important to the development of nanopore sized silica gel based chemical sensors [14]. This rate dictates the response time of the device and influences its sensitivity and selectivity. The rate, at which an entrapped receptor leaches from the matrix, is also important. This rate impacts the usability of the device and controls the time length that it can be used. Diffusion in silica materials will be more complex relative to diffusion in a liquid, as it will depend on the pore structure (pore size, pore size distribution, tortuosity) and the extent of the intermolecular interactions between the guest and the host [15]. Understanding how reagents move into and out of the sol–gel derived solid is vitally essential, as it offers the ability to control this process.

The response time of an ion-selective electrode is also an important factor for any analytical application. In the case of all electrodes, the average response time was defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference. The resulting potential-time responses for the mentioned electrode were obtained upon changing the Cu^{2+} concentration from 1.0×10^{-3} to 1.0×10^{-2} M (by fast injection of µl-amounts of a concentrated solution). Figure 3 clearly indicated that the potentiometric response time of the electrode was fast, less than 1 min.

E. pH Effect of the Test Solution

The potentiometric response of the membrane electrodes, based on the DPNSG, was found to be sensitive to the pH changes. When the same membrane electrode was conditioned in 1.0×10^{-4} M $Cu(NO_3)_2$ and 1.0×10^{-3} M $NaNO_3$ solution (for ~12 h), the electrode response was hardly affected by the pH change from 3.0 up to 6.0, implying that this electrode could be used to measure many environmental and industrial water samples without pH adjustment. However, outside this range, the electrode responses changed significantly. The decreased response at pH <3 seemed ascribable to the competitive binding of proton (or hydrated proton) to the ligands on the electrode surface. The diminished potential at pH>6.0 was due to some copper hydroxide formation in the sample solutions. In this pH range, neither the precipitation of the metal hydroxide nor the protonation of the dipyridyl group was expected.

F. Interference Studies

The potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the copper ion, Cu^{2+}, were determined by the matched potential method (MPM). The MPM is recommended by IUPAC [16] to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation [13, 16].

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (1.0×10^{-7} M copper nitrate, in this case) and the potential is measured. In a separation experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions.

The matched potential method selectivity coefficient, $K_{Cu,X}^{MPM}$ is then given by the resulting primary ion to the

interfering ion activity (concentration) ratio, $K^{MPM}_{Cu,X} = a_{Cu}/a_X$. The resulting values for the copper ion-selective electrode are listed in the text.

TABLE 3
POTENTIOMETRIC SELECTIVITY COEFFICIENT, $K^{MPM}_{Cu,X}$ (ELECTRODE **CPE3**).

Interfering Ion	Log $K^{MPM}_{Cu,X}$	Interfering Ion	Log $K^{MPM}_{cu,X}$
Cd^{2+}	-2.2	Cr^{3+}	-3.3
Hg^{2+}	-3.1	Co^{3+}	-3.5
Pb^{2+}	-3.0	Ce^{3+}	-3.4
Zn^{2+}	-3.2	Ag^{+}	-1.9
Ca^{2+}	-4.0	Tl^{+}	-3.0
Fe^{2+}	-3.1	Na^{+}	-4.0

From the data in this Table, it is quite obvious that this electrode is highly selective and sensitive with respect to other common cations. In most cases, the selectivity coefficients were in the order of 10^{-3} and lower (except for Ag^{+} and Cd^{2+}). The selectivity sequence of the employed dipyriyl-functionalized silica gel for different inorganic cations more or less obeys the order: $Cu^{2+} >> Ag^{+} > Cd^{2+} > Pb^{2+} \sim Tl^{+} > Fe^{+2} > Hg^{2+} > Zn^{2+} > Ni^{2+} > Cr^{3} > La^{3+} \sim Ce^{3+} > Co^{3+} > Ca^{2+} \sim Na^{+} > Mg^{2+} > K^{+} > Ba^{2+}$.

G. Lifetime

It is well-known that the loss of plasticizer, carrier or ionic site from the polymeric film, because of their leaching into the sample, is a primary reason for limited lifetimes of the carrier-based sensors. In principle, this shifts the involved equilibria for the ISEs and, therefore, should lead to a slow deterioration of selectivity and response. For the ISEs, the concentration decrease, if slow, would simultaneously occur at the membrane-inner filling solution interface. In this way, no net effect could take place in the measured potential, although the selectivity would still deteriorate. In contrast, the solid contact ISEs exhibited potential shifts due to leaching. The covalent immobilization of active components onto the polymeric backbone of the membrane is certainly one way to ensure a high lifetime of potentiometric sensors, especially for measurement of relatively lipophilic samples such as whole blood or organic solutions.

The lifetime of the DPNSG-modified electrode was studied by periodically recalibrating the potentiometric response to the Cu^{2+} ions in the standard copper nitrate solutions. After the conditioning step, the electrode was repeatedly calibrated three times every month. No significant change in the electrode performance was observed (Figure 4). This indicated that its lifetime was longer than nine months.

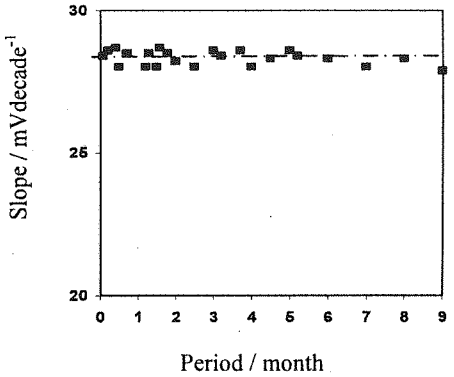


Figure 4: Slope of calibration plots for the copper electrode, based on the DPNSG (CPE3).

H. Analytical Application

As an application of the present electrode to a real sample, the quantitative determination and recovery of copper in waste water samples were carried out. Recovery studies were conducted with the sample containing various copper amounts. The calibration curve for waste water samples was also prepared using acetate solution. These calibration solutions contained copper in the range of 1.0×10^{-6} to 1.0×10^{-3} M and the buffer solution (10 mL standard copper solution were diluted with 2 mL buffer solution). The results of the recovery studies are listed in Table 4. The recoveries of the methods were in the range of 95-101% and 97-106% for waste water samples 1 and 2, respectively, which were produced from an electroplating factory in Tehran. The matrices of these samples contain heavy metal ions such as Ni^{2+}, Cr^{3+}, Cd^{2+}, Fe^{3+} and Pb^{2+}. It was displayed that the matrix of the waste water samples did not interfere significantly with the copper detection. CPEs modified with nanoporous silica gel, according to the design described in this paper, seem to provide an alternative device for the quantitative copper determination in environmental samples. Moreover, the copper content of one synthetic and two waste water samples were determined by the inductively coupled plasma technique (ICP). The results obtained by the DPNSG-modified electrode in combination with those obtained by ICP are depicted in Table 5. As it is derived from this Table, the determined copper concentration in these samples, using simple aqueous standard solutions for calibration, was in good agreement with the certified ICP method. These results demonstrated the applicability of the developed sensor with the employment of the functionalized silica gel for interference-free determination of copper traces in the analyzed environmental samples.

TABLE 4
COPPER RECOVERY FROM WASTE WATER.

Amount Added (M)	Waste Water Sample I Amout Found [a] (M)	Recovery%	Waste Water Sample II Amout Found [a] (M)	Recovery%
0	$7.6(\pm0.5) \times 10^{-6}$	---	$3.6(\pm0.3) \times 10^{-5}$	---
5.0×10^{-5}	$5.5(\pm0.4) \times 10^{-5}$	95	$8.3(\pm0.5) \times 10^{-5}$	97
4.5×10^{-4}	$4.6(\pm0.5) \times 10^{-4}$	101	$4.9(\pm0.3) \times 10^{-4}$	99
1.0×10^{-3}	$9.9(\pm0.6) \times 10^{-4}$	98	$1.1(\pm0.1) \times 10^{-3}$	106

[a] Average of three determinations

TABLE 5
DETERMINATION OF COPPER ION IN DIFFERENT SAMPLES.

Waste Water Sample	Concentration (M) Potentiometry [a]	ICP [a]
I	$7.6(\pm0.5) \times 10^{-6}$	$7.4(\pm0.4) \times 10^{-6}$
II	$3.6(\pm0.3) \times 10^{-5}$	$3.5(\pm0.3) \times 10^{-5}$
Synthetic	$7.3(\pm0.4) \times 10^{-4}$	$7.5(\pm0.3) \times 10^{-4}$

a Average of three determinations

I. Conclusions

The potentiometric method using the DPNSG doped in carbon paste electrode provided an attractive alternative for the Cu^{2+} ion determination. The electrode was easy to prepare, selective to copper over several heavy metals and presented a fast response time. Another unique feature of the recommended copper sensor was its good long-term stability (more than 9 months). This electrode demonstrated the importance of the organofunctionalized nanoporous silica gel in the development of potentiometric electrodes and its applicability for the determination of copper traces in the environmental samples.

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