Trace measurement of nickel in orthodontic cages with carbon paste electrode modified multi-walled carbon nanotubes by potentiometric method

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ABSTRACT

The utility of carbon paste electrode modified with 2-Amino acetophenone isonicotinoyl hydrazone (2-AAINH), for the potentiometric determination of Ni(II) in aqueous medium is demonstrated. The electrode exhibits linear response to Ni(II) over a wide concentration range (7.3×10^{-8}–9.1×10^{-2}) with Nernstian slope of 29 ± 0.5 mV per decade. It has a response time of about 50 s and can be used for a period of two months with good reproducibility. The detection limit of this electrode was 5.0×10^{-7} M. The proposed electrode shows a very good selectivity for Ni(II) over a wide variety of metal ions. This chemically modified carbon paste electrode was successfully used for the determination of Ni(II) in electronics waste sample solution.

INTRODUCTION

The universal ion selective liquid-state electrode based on carbon was introduced by Ruzicka et al. in 1970 [1–3]. These electrodes have a thin layer of organic material (the active species) on graphite rod which is mounted into the teflon tube. Ion selective electrodes containing spectral graphite power, nujol oil and metal salts of low solubility in a plastic body were described by Mesaric and Dahmen in 1973 [4].

The application of chemically modified electrodes (CMEs) in analytical chemistry has attracted considerable attention. A few numbers of CMEs have been demonstrated as potentiometric sensors [5–7] in 1978 and 1979. In 1980 Heineman et al. [8] described the first use of a polymer film chemically modified elctrode as a potentiometric sensor.

Essential to living organisms in small doses, but it can be very dangerous when the maximum tolerable amounts are exceeded [9-11]. Nickel is mostly used as an ingredient of steel and other metal products. Also, nickel products such as nickel-based catalysts have an important role in the reactions between organic compounds [12-18].

A number of methods [19-24] such as atomic absorption spectrometry (AAS), atomic absorption spectrometry electrothermal atomization (AAS-ETA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and flame photometry can be used for determination of nickel.

These methods generally require sample pretreatment and infrastructure backup; therefore, are not very convenient for routine analysis of a large number of environmental samples. Thus, there is a critical need for the development of selective, portable, and inexpensive diagnostic tools for the determination of nickel. Many optical chemical sensors utilize colored complexes [25,26] or redox reagents [27,28] immobilized in a suitable matrix.

Potentiometric electrodes based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivffity, sensitivity, good precision, simplicity, and low cost. This work is to introduce a very simple and inexpensive (potentiometric) method in determination of nickel(II) in a wide concentration range. In this study, Ni (II) carbon paste electrode (CPE) based on *2-AAINH* ionophore, Fig1, was constructed in order to determine Nickel ion concentration. Then the electrode was modified by MWCNTs to achieve the better electrode response. The modified electrode was successfully used as an indicator for potentiometric determination of Ni (II) in aqueous sample.

REAGENTS AND CHEMICALS

The reagent, 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) was synthesized by condensing equimolar solutions of 2-amino acetophenone and isonicotinoyl hydrazide in alkaline absolute ethanol as described earlier.

1×10^{-2} M solution of 2-AAINH was prepared by dissolving 0.351 g of the crystallized compound in dimethyl formamide and diluting to 100mL. Lower concentrations were prepared by diluting the stock solution appropriately with the solvent. Stock solution of nickel (2×10^{-2}M) was prepared by dissolving of $NiSO_4.7H_2O$ (Merck) in doubly distilled water. Lower concentrations were prepared by diluting the stock solution appropriately with distilled water.

The buffer solutions were prepared by mixing appropriate volumes of 0.2M sodium acetate and 0.2M acetic acid (pH 3.0 to 7.0) and 3.0 M ammonium hydroxide and 3.0 M ammonium chloride (pH 8.0 to 10.0). The pH of these buffer solutions was finally adjusted to the required value by using pH meter. The multi-walled carbon nanotubes (MWCNTs) with 10–40 nm diameters and 1–25 μm length were purchased from Research Institute of the Petroleum Industry (Iran).

Apparatus

The glass cell in which carbon paste electrode was placed into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode. The Ni^{2+} CPE was used as an indicator electrode.

Both electrodes were connected to a pH/mV meter (Metrohm-691, Switzerland). The following cell was assembled for the conduction of the EMF (electromotive force) measurements:

Carbon paste electrode | sample Ni^{2+} ion solution | Ag/AgCl–KCl (satd.)
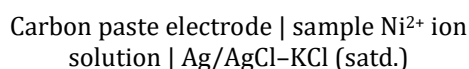
Electrode Preparation

General procedure to prepare the carbon paste electrode was as follows: Different amounts of 2-Amino acetophenone isonicotinoyl hydrazone as an ionophore with an appropriate amount of graphite powder, Plasticizer (DBP) and MWCNTs were thoroughly mixed. After homogenization of the mixture, the paste was thoroughly packed into the teflon tube and a electrice wire was inserted into the opposite end of the CPE to set up electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 24 h by soaking it in a 1.0×10^{-3} mol L^{-1} $Ni(NO_3)_2$ solution.

RESULTS AND DISCUSSION

Carbon paste electrode composition

The sensing element of a potentiometric ion-selective electrode has important role in selectivity behavior of the electrode. The influence of the percent of materials in the carbon paste composition was investigated and the results are summarized in Table 1. The typical CPE with optimized composition (electrode no.2) shows a Nernstian slope of 29.3 mVper decade. The electrode composed of 14%paraffin oil, 4% Ionophore, 72% Graphite powder, 5% Plasticizer and 5% MWCNT was found to be optimal for Ni^{2+} carbon paste electrode. These results show that the 2-AAINH is an excellent ionophore for Ni^{2+} ion, also, addition of MWCNTs to the paste improves the linear range and the response time of the electrode. This new carbon paste electrode was selected for further examination.

Measuring range and detection limit

The response of the optimal modified Ni^{2+} carbon paste electrode (no.5) was tested across Ni^{2+} ion concentration range of 7.3×10^{-8}–9.1×10^{-2} mol L-1. The applicable range of the proposed sensor extends from 7.3×10^{-8}–9.1×10^{-2} mol L^{-1} as seen in Figure 1.

Table 1. The optimization of the carbon paste ingredients

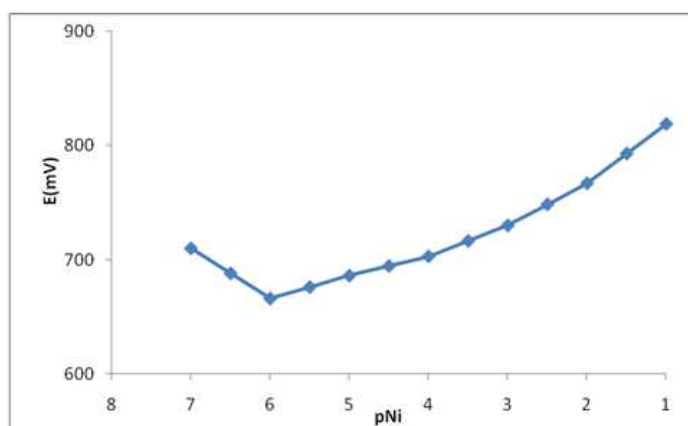| NO	Composition of Carbon Paste (wt. %)					Slope (mV/decade)	Dynamic linear range
	Paraffin oil	Ionophore	Graphite Powder	MWCNTs	Plasticizer		
1	18	4	70	5	3	24.88	1.4×10^{-5}-1.4×10^{-1}
2	10	3	64	3	20	28	1.5×10^{-6}-1.0×10^{-1}
3	12	4	70	3	12	24.8	1.0×10^{-4}-1.0×10^{-1}
4	14	4	72	5	5	25.1	1.4×10^{-8}-1.0×10^{-1}
5	14	4	72	5	5	29.5	7.3×10^{-8}–9.1×10^{-2}
6	11	4	64	4	17	28.8	1.0×10^{-6}-1.5×10^{-1}
7	10	3	68	3	16	28	1.0×10^{-5}-1.0×10^{-1}
8	10	4	65	3	15	29.1	1.2×10^{-6}-1.0×10^{-2}

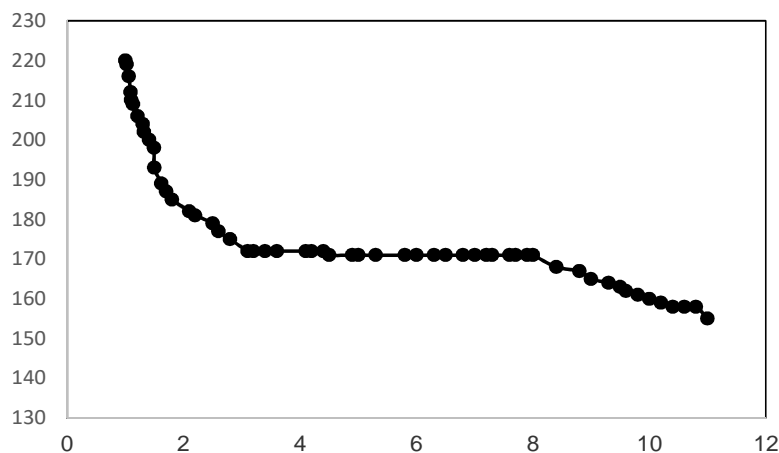**Figure 1. Calibration curve of N^{i2+} carbon paste electrode (Electrode no.5)**

Figure 2: Effect of pH on the potential response of the Ni2+ carbon paste electrode in the test solution of Ni^{2+} ion (10^{-3} mol L^{-1})

rather irregularly with increasing analyte acidity. At such high acidic solutions, the observed increase in potential indicates that the protonated ionophore possesses a poor response to the Ni^{2+} ions and strong response to H3 O+ ions in the solution. As can be seen in Figure 2the potential decreased sharply at higher pHs (>8) due to the formation of Ni (OH)$_2$ which not reacts with the ligand. In addition, Fluctuations at pH greater than 8 might be due to the formation of soluble or insoluble Ni^{2+}

pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Ni^{2+} sensor (no.5), the potential was measured for a fixed concentration of Ni^{2+} ion solutions (10^{-3} mol L^{-1}) at different pH values. The pH was varied from (1-14) by addition of concentrated HNO_3 or NaOH. The change in potential as a function of pH is shown in Figure 2. The potential was constant and quantitative in the pH range of 3.0-8. At pH<3.0, the electrode response increased

electrode's specificity toward the target ion in the presence of interfering ions, the potentiometric selectivity coefficients of the proposed carbon paste electrode were evaluated by separate solution method (SSM) [28] and the results are depicted in Table 2.

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion (A) at the activity aA, the other one containing the ion (B) at the same activity $aA=aB$. If the measured values are EA and EB, respectively, the value of is calculated from the equation:

$$\log KA,Bpot=(EB-EA)\frac{ZAF}{2.30RT}+(1-\frac{ZA}{ZB})\lg aA$$

These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

hydroxy complexes. The fluctuations at a pH value of 3.0 were attributed to the protonation of ligand in the carbon paste.

Response time

Response time is an important factor for any sensor. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. The measurements of potential versus time were carried out with the Ni(II) nitrate solutions from lower (1.0×10^{-6} M) to higher (1.0×10^{-1} M) concentrations (Figure3). For the proposed modified Hg^{2+} sensor, the response time was less than 5s.

Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective
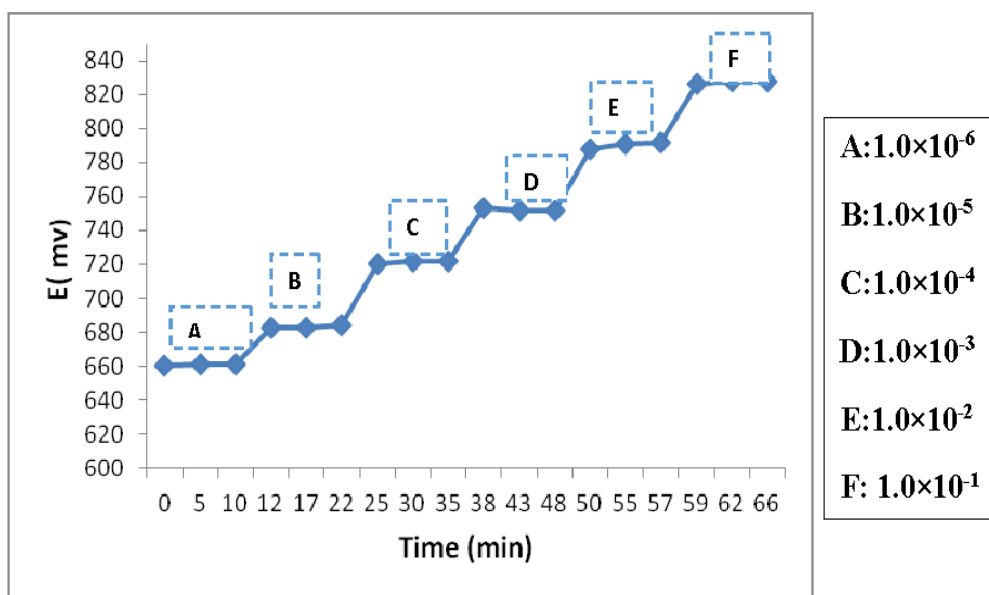

Figure 3: Dynamic response time of the proposed carbon paste electrode (no.5)

Table 2: Selectivity coefficients of various interfering species for proposed sensor

Interfering ions	K_{ij}^{pot}	Interfering ions	K_{ij}^{pot}
Mg^{2+}	2.4×10^{-3}	Zn^{2+}	1.2×10^{-3}
Co^{2+}	1.4×10^{-3}	Ag^+	1.2×10^{-3}
Sn^{2+}	1.4×10^{-3}	Li^+	1.2×10^{-2}
Cu^{2+}	1.4×10^{-3}	Fe^{3+}	1.3×10^{-3}
Cd^{2+}	2.2×10^{-3}	Cr^{3+}	3.1×10^{-3}
Mn^{2+}	2.3×10^{-3}		

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Table3: Recovery of copper ions from different water samples.

Sample	Ni²⁺ added	Ni²⁺founded	RR%	RSD% (n=3)
Sample 1	3×10^{-5} M	2.76×10^{-5}	92.2	2.15
Sample 2	3×10^{-5} M	2.74×10^{-5}	92.4	1.831

Quantification, accuracy and precision

One gram of the dry and clean orthodontic cages sample was dissolved in minimally concentrated nitric acid and the solution was transferred to a 100 ml of calibrated flask and diluted to the mark with distilled water. The pH of solution was controlled and the measurement was done. With the use of sensor's calibration curve, the nickel content in our sample, obtained from triplicate measurement with electrode that was in satisfactory agreement with that determined by atomic absorption spectrometry 2.76×10^{-5} M **and** $2.74 \times 10^{-}$M

The proposed methods were used for direct potentiometric determination of investigated orthodontic cages, which was performed and calculated from calibration graph. Table 3 indicates that the results obtained by this method are in good agreement, however, the proposed method is more selective, simple and less time consuming. The results, in **Table 3**, show an average recovery of 92.4% with relative standard deviation (RSD) of 1,83%. The results of this study confirm that the sensor can be successfully used for routine analysis with portable equipment.

CONCLUSION

In this work, Ni²⁺ carbon paste electrode based on MWCNT 2-Amino acetophenone isonicotinoyl hydrazone as ionophore is introduced. By incorporating ionophore in composite of this electrode, high selectivity and sensitivity to copper ion were observed. The modified CPEs show better potentiometric response than typical CPEs in terms of sensitivity, Nernstian slope, linear range, and response stability. Since the electrode shows excellent sensitivity, selectivity and stability, it may find application in the analysis of real samples. The electrode has a great potential to be used in the development of portable analyzers for monitoring Ni (II) ions in very polluted natural waters.

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