

Highly sensitive carbon paste electrode with silver-filled carbon nanotubes as a sensing element for determination of free cyanide ion in aqueous solutions

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Abstract We report on newly synthesized Ag(I)-filled multiwall carbon nanotubes as a potential sensing element in ion-selective carbon paste electrodes for the determination of free cyanide in aqueous solution. The electrode was obtained by entrapping the silver-filled nanotubes into a carbon paste and displays a Nernstian response with a slope of 59.8 ± 0.3 mV decade⁻¹, a very wide linear range (from 21.0 nM to 0.1 M of cyanide), a lower detection limit of 13.0 nM, and a response time of <2 min. The operational lifetime is up to 3 months without significant deviation in normal function.

Keywords Carbon past electrode · Cyanide ion · Filled nanotube · Ion-selective electrode · Silver(I)

Introduction

Cyanide is one of the most toxic chemical substances on Earth and is toxic to most aquatic life and humans, even at low concentrations. The importance of cyanides in technological and industrial fields is well known from using to extract gold and silver from their mines to key role as constituents of amino acids in animal and plant structures [1–3]. The high degree of toxicity that these compounds

present to living organisms alone warrants their study [2–4]. Some procedures have been reported for measurement of cyanides, which generally suffer from high experimental steps, unfavorable precision, low accuracy, and demand for fast operations [4–12].

Carbon paste electrodes (CPEs) are widely used in various electrochemical applications due to their simplicity, wide potential range for analysis, non-toxic character, easily preparation and easy surface renewing [13–16]. Furthermore, all contacts in this type of electrode are solid-state which provides maintenance-free towards common ion sensors to eliminate the inner filling solution. Various electrochemical detection schemes have been reported by employing different inorganic and organic modifiers in carbon pasts [17–22]. Although considerable attention has been given to preparation of CPEs so far, the applications of these CPEs mainly have been focused on the field of voltammetric determination and only few of these types of the electrodes have been used in potentiometry.

Among modifiers, carbon nanotubes (CNTs) have become the most outstanding material in most recent works on the determination of chemical species employing CNTs as sensing materials because the unique properties of CNTs make them very attractive for operation of chemical sensors in general, and electrochemical detection in particular [23–26]. On the other hand, substances that are incorporated into the channels of CNTs can take part in chemical reactions. Filling of CNTs with proper species has recently become a very interesting field in nanotube science. This can be accomplished either during or after their synthesis. By thermal decomposition of oxides and their reduction, metal-containing nanotubes were obtained [27]. The inner spaces of tubes could be filled by chemical deposition from the gas phase by utilizing, e.g., volatile metal compounds [26, 28].

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So far, to the best of our knowledge, there is no report on the study of filled CNTs used in CPEs. This is the first report on construction a carbon paste selective electrode based on a filled CNTs by potentiometric method. In addition, this is the first report on determination of highly toxic cyanide ion by the proposed system. Few reports for determination of cyanide by CPEs are available in literature [29–31]. In this study, we are describing the use of a newly synthesized Ag(I)-filled-multiwall carbon nanotube (Ag-MWCNT) as a sensing ion-selective element in the construction of a novel CPE for determination of free cyanide ion in aqueous solution.

Experimental

Reagents

Graphite powder and paraffin oil were purchased from Fluka (www.sigmaaldrich.com), Switzerland. Multiwall carbon nanotubes (MWCNT), filled with Ag(I), prepared as described elsewhere [32]. Sodium and potassium of all anions were of analytical reagent grade from Merck (www.merck-chemicals.com). Solutions were prepared with doubly distilled and deionized water.

Apparatus

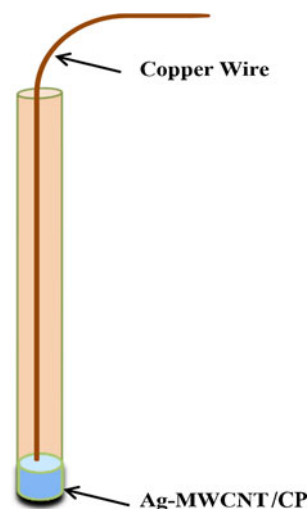
All potentiometric measurements were recorded on a CRISON BASIC 20 (www.crison.es, Spain) pH/mV-meter. The reference electrode was a silver/silver chloride electrode. A Jenway pH-meter (UK 3020, www.jenway.com) was used for pH measurements. All potentiometric measurements were carried out by using the following assembly.

Ag/AgCl(sat'd)||test solution|(Ag – MWCNT)/CPE

Preparation of Ag-MWCNT/CPE

The ion selective electrode was prepared by mixing 4 mg Ag-MWCNT and 80 mg pure graphite powder, which was completely mixed to obtain a homogenized powder. Then, 50 mg of Paraffin oil was added to the mixture and mixed fully until it was uniformly wetted. Subsequently, the carbon paste (CP) was packed into a polypropylene electrode holder (inner diameter of 3 mm) and the electrical contact was established with a copper rod through the back of the electrode (Fig. 1). Before using, the electrode surface was polished by a page of paper contaminated with alumina powder to produce a reproducible working surface.

Fig. 1 Structure of the Ag-MWCNT/CPE with incorporated Ag-MWNT as a sensing element



Measuring procedure

The electrodes were immersed directly into the test solutions. A citrate buffer (0.015 M) was used to adjust the pH of the solutions at 10.0 ± 0.1 . Then proper amounts of potassium cyanide solution were added to the test solution and temperature was controlled at 20.0 ± 0.1 °C with a water-circulating bath system. The solution was stirred immediately until the response of the system reached constant (about 2 min). The potentiometric data was gathered after each cyanide solution addition versus the reference electrode. Highly toxic cyanide ion can be adsorbed on the walls of glass vessels, so all experiments were carried out in a polyethylene beaker.

Results and discussion

As reported by [30], the Ag^+ ion and its nitrate counter ion are in the MWCNT channel where the electrostatic ionic forces are operating. This fact could be due to the requirement for electro-neutrality of the system. It would be a good idea if we provided an optimal condition in which the nitrate ion be exchanged with another proper ion [33–35]. This is the basic idea to prepare a CPE for which nitrate anion could be replaced by cyanide ion in an exchange fashion at the electrode-solution interface. Visualization of such a mechanism is demonstrated in Fig. 2.

It is well known that several parameters must be considered during the development of a useful ion-selective electrochemical sensor.

Effect of composition

Influence of carbon paste and membrane compositions on the ISEs' performances are crucial. Thus, different aspects of the composition of the proposed CPE based on Ag-

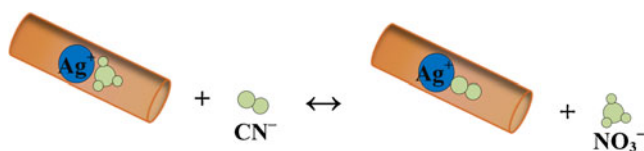


Fig. 2 Visualization of the exchange fashion of sensing element Ag-MWCNT in which nitrate anions could be replaced by cyanide ions at the electrode-solution interface

MWCNT were optimized for determination of cyanide ion. For this purpose, some electrodes with different compositions of basic compounds were prepared. The used ratios of the reactants showed that the corresponding slopes and dynamic ranges of response calibration curves were closely depended on the proportion of the modifier in the electrode. According to the results that are shown in Table 1, there was no considerable response for the electrode in which no sensing element was used (No. 1). The effect of the amount of Ag-MWCNT on the electrode performances were investigated (Nos. 2–4). Electrodes 3, 5 and 6 are showing the influence of the paraffin ratio on the electrode response. Electrodes 3, 7 and 8, demonstrate the graphite effect. From this table, optimum amounts of the reactants are 4:50:80 (mg, No. 3) for Ag-MWCNT: paraffin:graphite, respectively.

Response time of proposed electrode

From the literature and our preliminary experiments, the response time value ($t_{95\%}$) of the sensor, when reaches to 95% of its final value (steady state), depends on the sensing membrane composition [36]. The electrode response time was evaluated by measuring the average time while it was in a 10^{-4} M solution of cyanide ion. Reading the response potential was started from the time of addition of cyanide solution to the time after which the electrode response reached a steady state, for which the results are plotted in Fig. 3. This time (<2 min) was evaluated from the

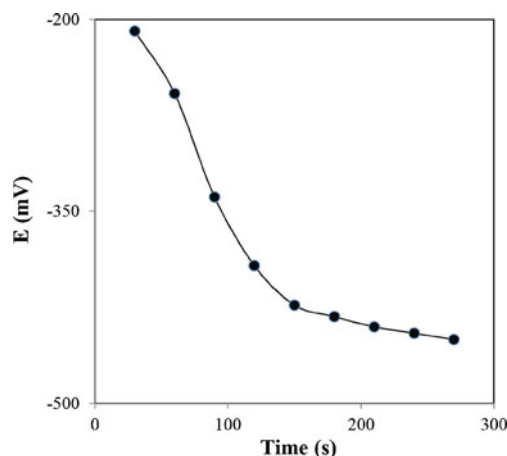


Fig. 3 Plot of potential responses of the electrode (No. 3) versus time. The electrode responses are constant after 2 min

intersection of the two extrapolated segments of the response time curve (by creating proper regression equations from the data). Thus, the response time of 2 min was used for subsequent potential readings.

Effect of pH

As an important factor, pH value influences the determination of cyanide ion directly. Cyanide is a strong base ($pK_b = 4.79$) and at pH values below 9.5, cyanide species is converted into a volatile and highly toxic weak acid, HCN. Thus, the effect of pH on the potential response of the electrode (No. 3) was evaluated from a fixed concentration of CN^- (1.0×10^{-4} M) in the solution at different pH values. The desired pH was adjusted by adding small volumes of concentrated hydrochloric acid or sodium hydroxide solutions to the test solution and the variation of potential was followed after each addition. The potential variations were plotted as a function of pH, as seen in Fig. 4. From this figure, the response of the electrode remains unchanged in the pH range of 8–12 and the electrode works satisfactorily

Table 1 The results of optimization of composition of the proposed electrode

Composition (mg)				Performances		
No.	Ag-MWCNT	Paraffin	Graphite	Slope (mV/dec)	DL (M)	Linear working range (M)
1	0	50	80	–	–	–
2	3	50	80	54.9	2.8×10^{-7}	$3.3 \times 10^{-6} - 1.3 \times 10^{-1}$
3	4	50	80	59.8	1.3×10^{-8}	$2.1 \times 10^{-8} - 1.0 \times 10^{-1}$
4	5	50	80	56.3	4.0×10^{-7}	$6.1 \times 10^{-7} - 7.1 \times 10^{-1}$
5	4	40	80	58.1	3.1×10^{-7}	$5.3 \times 10^{-7} - 1.1 \times 10^{-1}$
6	4	60	80	49.2	3.6×10^{-6}	$5.0 \times 10^{-6} - 2.1 \times 10^{-1}$
7	4	50	70	57.3	4.2×10^{-7}	$8.4 \times 10^{-7} - 2.2 \times 10^{-1}$
8	4	50	90	54.2	2.4×10^{-6}	$4.4 \times 10^{-6} - 2.1 \times 10^{-1}$

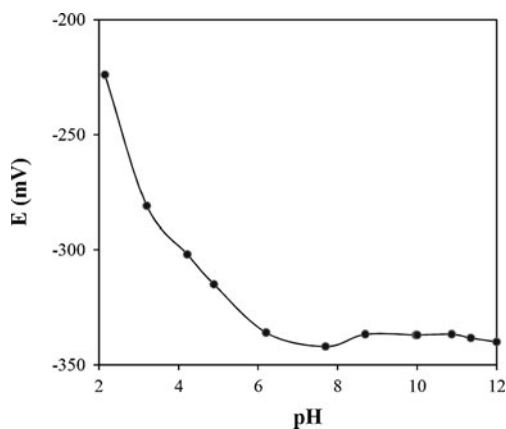


Fig. 4 The plot of potential variations of electrode No. 3 as a function of pH of the solution

in this pH range. At pH values lower than 8 the response of the electrode influences from the pH of the solution tested that can be due to HCN formation and reduction of free cyanide mole fraction. So pH=10.0, which was prepared from citric acid/sodium citrate buffer solution (0.015 M), was used as an optimum pH in subsequent potentiometric measurements.

Analytical performances

The critical response characteristics of the cyanide—selective electrode (No. 3) were investigated according to IUPAC recommendations [37, 38]. A series of standard solutions of CN^- were examined by the electrode. The potential responses of the electrode at varying CN^- concentrations follows a linear trend for concentrations ranging from 2.1×10^{-8} to 1.0×10^{-1} M with a near-Nernstian slope of 59.8 ± 0.3 mV decade $^{-1}$, which are demonstrated in Fig. 5.

The detection limit (DL) was estimated to be 1.3×10^{-8} M of CN^- which was evaluated from the intersection of the two extrapolated segments of the above calibration plot at the lowest portion.

In order to obtain a comparison between the behaviors of the electrode (No. 3) toward some common anions and cyanide ion, the electrode performances were separately examined in the presence of some other sodium salts of anions such as thiocyanate, chloride, iodide, hydroxide and acetate. As shown in Fig. 6, the electrode response to cyanide ion is reasonably quantitative.

The selectivity power of the system was investigated by estimating potentiometric selectivity coefficients for different anions by using fixed interference method [38–40]. The potential responses of a cell including the ISE and a reference electrode (Ag/AgCl) were measured for solutions of constant activity of the interfering ion (0.01 M), a_B , and varying activity of the primary ion, a_A . The obtained

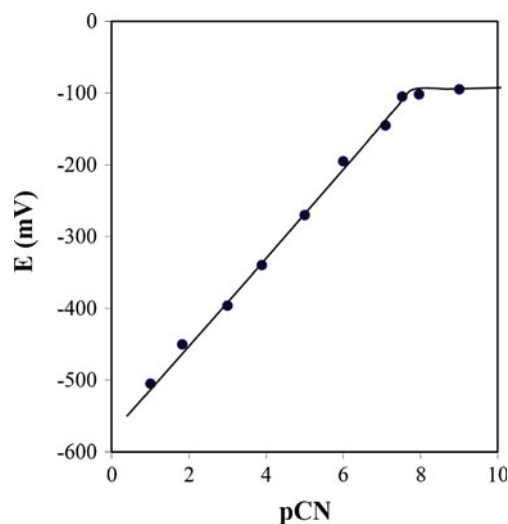


Fig. 5 The potential responses of the electrode (No. 3) at varying CN^- concentrations (1.1×10^{-9} to 1.0×10^{-1} M) in the solution. The plot follows a linear trend for concentrations ranging from 2.1×10^{-8} to 1.0×10^{-1} M with a slope of 59.8 mV/decade

potential values were plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicated the value of a_A to calculate selectivity coefficients from the following equation (Eq. 1):

$$K_{A,B}^{pot} = \frac{a_A}{a_B^{(z_A/z_B)}} \quad (1)$$

where z is the charge of ion. The results are summarized in Table 2. From this table, it is obviously seen that the cyanide—selective electrode is quite selective with respect to some chemical species were tested to check their levels

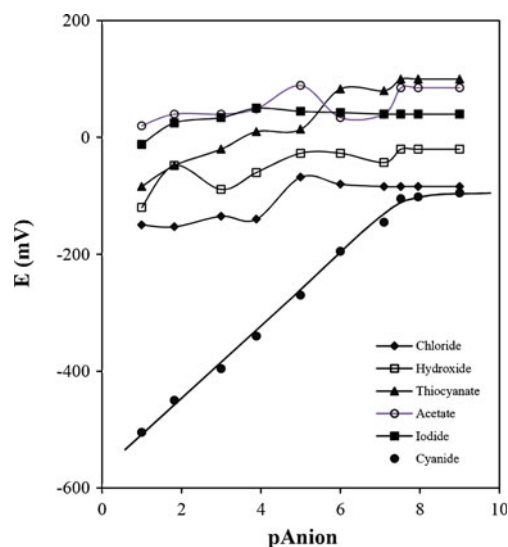


Fig. 6 Plot of potential responses of the electrode (No. 3) toward some common anions to comprise with the electrode response to cyanide ion in the solution

Table 2 Selectivity coefficients ($K_{A,B}^{pot}$), of various interfering anions

A^{n-}	$K_{A,B}^{pot}$	A^{n-}	$K_{A,B}^{pot}$
Cl^-	4.2×10^{-3}	I^-	3.8×10^{-3}
Br^-	3.1×10^{-3}	$C_2O_4^-$	2.2×10^{-3}
SCN^-	9.2×10^{-3}	NO_3^-	1.0×10^{-4}
CH_3COO^-	1.5×10^{-3}	SO_4^{2-}	3.4×10^{-4}
HPO_4^{2-}	2.2×10^{-3}	ClO_4^-	5.5×10^{-4}
CO_3^{2-}	3.4×10^{-3}		
NO_2^-	5.2×10^{-4}		

of interference in cyanide determination. Table 2 also shows that the selectivity coefficients are small enough for all tested diverse ions indicating they would not significantly disturb the functioning of the modified electrode, so it possesses a high selectivity. This highly selective behavior of the electrode toward CN^- could be attributed to the capability of Ag^+ ion to form well-known complex(es) with CN^- as $AgCN_2^-$ and $Ag[AgCN_2]$.

The practical reversibility and precision required for the sensor, to reach a potential within ± 1 mV of the final equilibrium value, were investigated. This was evaluated by potential reading for the electrode dipped alternatively into two different solutions of cyanide ion 1.0×10^{-3} and 1.0×10^{-5} M, respectively. Six potentiometric experiments were repeatedly carried out with the same CPE. The resulted relative standard deviations (RSDs, (%)) of ± 0.5 and ± 0.7 were calculated for the lower and the upper CN^- concentrations (for 15 replicate measurements), respectively. These RSDs show that the electrode had unchanged its sensing behavior while the potentials were being recorded either from the low to the high concentrations or vice versa. The results are demonstrated in Fig. 7. Furthermore, the system

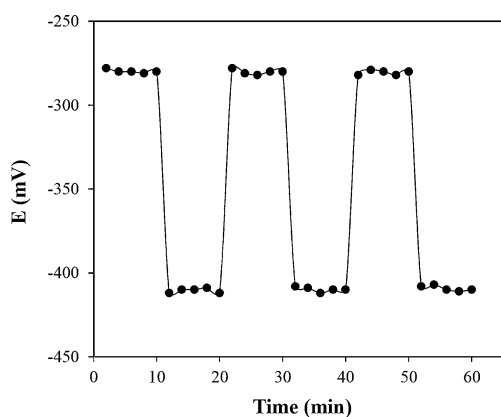


Fig. 7 Six repeatedly carried out potentiometric experiments with the same Ag-MWNT/CPE. The data was evaluated by potential reading for the electrode (No. 3) dipped alternatively into two different solutions of cyanide ion 1.0×10^{-3} (bottom) and 1.0×10^{-5} M (top), respectively

responses are reasonably repeatable over the potentiometric measurements. As this figure reveals, the electrode potential responses are quite reversible for reading the potential of each solution.

Reproducibility of the system was tested when several electrodes with the same compositions were immersed in the same standard solution of cyanide ion. The responses were nearly the same (within ± 5 mV) which indicate there is a good reproducibility.

The lifetime of the modified electrode was also tested over a period of 3 months. During this period, the electrode was in daily use over extended period of time (1 h a day) and only a small decrease of potential sensitivity (less than 4%) for 1.0×10^{-4} M CN^- was observed, which can be attributed to the excellent stability of the sensor.

As can be realized from the above-mentioned characteristics of the optimized electrode, a Nernstian response, low DL, a wide calibration range with good reversibility and reasonable reproducibility are the suitability of this electrode to determine the cyanide free ion, within the offered concentration range, in solution.

Applications

Samples of aqueous solutions including cyanide ion were collected from different sources, an electroplating manufactory waste, a photographic film development waste solution and a cyanide added tap water. After filtration to remove suspension solids and some organic substances the concentration values of CN^- in the samples were determined by using the proposed method. The cyanide contents of the samples were also determined by a standard spectrophotometric method [11]. The concentration values obtained from both methods (for six repeated measurements, $n=6$) were listed in Table 3. Obvious differences were not found between the results obtained by the electrode and the standard spectrophotometric method. Furthermore, the evaluated RSDs, average 0.80% for all measurements in Table 3, are small enough (comparable with the standard method, 1.0%) which are expected for such valuable potentiometric electrode.

Table 3 Cyanide content (ppm) of some aqueous samples ($n=6$)

Sample	Ag-MWNT/CPE	Spectrophotometric Method
Electro-plating waste water	220.3 ± 1.1 (0.5) ^a	224.3 ± 2.1 (1.0)
Photographic film developing waste water	35.3 ± 0.7 (2.0)	36.1 ± 0.4 (1.1)
Cyanide-added tap water	10.3 ± 0.3 (2.9)	10.1 ± 0.2 (2.0)

^a Values given in the parentheses are RSDs%.

Conclusions

In this work, we applied a modified carbon paste electrode (MCPE) for determination of free cyanide anion in aqueous solution using potentiometric method. According to our knowledge, this is the first report on cyanide selective electrode based on the chemically MCPE using potentiometric method. Not only the method is simple and inexpensive, the electrode has the advantages of being selective for cyanide in the presence of variety of anions such as SCN^- , Γ^- , Cl^- , Br^- and oxalate that usually are serious interfering species for most of cyanide ISEs. In addition, application of a new type of materials, a silver(I)-filled carbon nanotube develops the area of employment of modified CNTs as sensing elements in ion selective devices and promising applications in analytical chemistry for constructing CNT-based sensors.

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