

Research Article

Modification of Multiwalled Carbon Nanotubes by Dipyrindile Amine for Potentiometric Determination of Lead(II) Ions in Environmental Samples

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A carbon paste electrode was modified by dipyrindile amine functionalized multiwalled carbon nanotubes for determination of trace amounts of lead(II) ions. The electrode composition was graphite powder 70%, paraffin 23%, and dipyrindile amine modified MWCNTs 7% (W/W). The linear range for lead(II) was 9.5×10^{-8} to 2.5×10^{-3} mol L⁻¹, and the limit of detection was obtained 7.0×10^{-8} mol L⁻¹. The lifetime of the electrode was ten weeks, and a fast response time was observed. The electrode was used for determination of trace amounts of Pb(II) ions in real samples and standard reference materials of water, soil, and plant.

1. Introduction

As the industries have become widespread, pollution has become a big concern all over the world [2, 3]. Determination of heavy metals in environmental samples plays an important role in the monitoring of environmental pollution [4, 5]. Lead is one of the heavy metals which has attracted lots of researchers interest in environmental protection due to its toxicity [6]. World Health Organization (WHO) has announced the critical level of Pb(II) ions less than $10 \mu\text{g L}^{-1}$ which shows its high toxicity [7]. Continuous exposure to Pb(II) ions causes dangerous effects to human brain, blood, kidneys, and nervous and reproductive system [8]. Using lead in gasoline antiknock products and paint pigments are the two most widespread uses of this heavy metal. Also it is used in storage batteries, cable sheaths, solder, and radiation shielding [9]. Being an increasing element in environment and being toxic and harmful even at low concentrations are the reasons of developing new methods for determination of lead in environmental samples. There are lots of methods for the determination of Pb(II) ions in natural samples such as atomic emission spectrometry [10], fluorescence

spectrometry [11], potentiometric stripping analysis [12], mass spectrometry [13], and inductively coupled plasma optical emission spectrometry (ICP-OES) [14]. Among these methods, potentiometric methods using ion sensors are common due to their accuracy, high rate, and low cost and also being nondestructive [15]. Potentiometric carbon paste electrodes (CPEs), in comparison to polymeric membrane electrodes, possess very attractive properties such as ease of preparation, renewable surface, stability of their response, low ohmic resistance and no need for internal solution [16, 17]. Introduction of a chemical modifier causes preconcentration of ions on the electrode and increases the methods sensitivity and decreases the detection of limit value [18]. Owing to interesting properties such as ordered structure with high aspect ratio, high surface area, high mechanical and thermal stability, and high electrical conductivity, the usage of carbon nanotubes (CNTs) has been increased recently [19–25]. However, in order to be selective, the CNT needs to be modified with an appropriate ligand [26]. In this work, for the first time, multiwalled carbon nanotubes have been modified with dipyrindile amine group and used in a sensor for fast determination of Pb(II) ions in environmental samples. This

method was validated using several standard reference materials with certified amount of Pb(II) ions. Also this method was applied for determination of Pb(II) in natural samples and the results were compared with a previously established method using inductive coupled plasma spectroscopy.

2. Experimental

2.1. Regents and Solutions. All analytical grade reagents were persuaded from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland) and used without further purification. 2,2'-dipyridylamine was purchased from Sigma-Aldrich company (Missouri, United States). Paraffin oil and lead nitrate were persuaded from Fluka. Carboxyl modified multiwalled carbon nanotube (COOH-MWCNT) with 30 μm length and 5–10 nm in diameter was purchased from Neutrino Company (Tehran, Iran). All other chemicals were purchased from Merck Company and used without further purification. All solutions were made using deionized water, provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system.

2.2. Preparation of Dipyridile Amine Functionalized Multiwalled Carbon Nanotube. For synthesis of dipyridile amine functionalized multiwalled carbon nanotube, in a 250 mL two-neck round-bottom flask, equipped with a magnetic stir bar and a reflux condenser, 1.0 g of COOH-MWCNT was suspended in 50 mL of dried CH_2Cl_2 under nitrogen atmosphere. To this solution 10 mL of oxalyl chloride was slowly added from a dropping funnel. After stirring for 24 h, CH_2Cl_2 was removed under reduced pressure, and the residue was suspended again in 50 mL of dried methanol. Then 5 mL of triethylamine and 1 g of dipyridile amine were added to reaction mixture. After stirring the mixture for 24 h at room temperature, methanol was removed under reduced pressure and the sorbent was dried at 80°C under vacuum. The formation of dipyridile amine functionalized multiwalled carbon nanotube was confirmed by IR spectroscopy, elemental analysis, SEM micrograph, and thermal analysis. A schematic diagram of this synthesis is represented in Figure 1.

2.3. Instruments. A R684 model Analion Ag/AgCl double-junction reference electrode was used as a reference electrode. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements. The pH meter was a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. All measurements were made at $25 \pm 1^\circ\text{C}$. Thermal gravimetric and differential thermal analysis (TG/DTA) was carried out on a Bahr STA-503 instrument (Germany) under air atmosphere. IR spectra were recorded by BOMEM/MB series Spectrometer (Quebec, Canada). The Elemental analysis was performed with a Thermo Finnigan Flash-2000 microanalyzer (Neolab, Italy). Morphology and size of the particles were observed on a Philips S-4160 scanning electron microscope (SEM) (Eindhoven, The Netherlands) with gold coating.

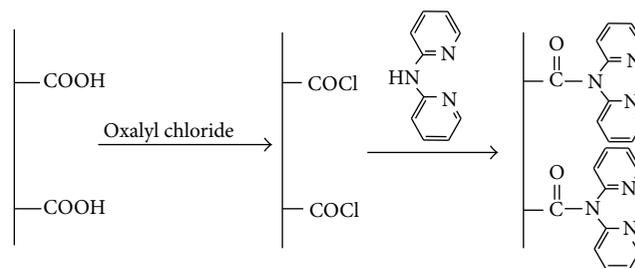


FIGURE 1: A schematic diagram for modification of MWCNT with dipyridile amine.

2.4. Preparation of Modified Carbon Paste Electrode. The chemically modified carbon paste electrodes were prepared by thoroughly mixing a mixture that contains graphite powder 70%, paraffin 23%, and dipyridile amine modified MWCNTs 7% (W/W). 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 a soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste.

2.5. Electrode Conditioning. The electrode surfaces were conditioned by $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$ and $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ NaNO}_3$ for 24 hours. The pH of the solution was adjusted to 6 by acetate buffer (0.01 mol L^{-1}). The electrodes were rinsed by deionized water before potentiometric measurements.

2.6. Emf Measurements. All measurements were done versus Ag, AgCl(s) reference electrode. The pH was adjusted to 6 by acetate buffer with concentration of 0.01 mol L^{-1} .

The electrochemical cell can be represented as follows:

Ag, AgCl (s), KCl (3 mol L^{-1}) || analyte solution | carbon paste electrode.

2.7. Sample Preparation. A drinking water sample (ERM-CA022) was obtained from Chemistry Reference Laboratory Equipment (Turkey) and used without any treatment. Water samples were obtained from tap water (Tehran, Iran), distilled water, and sea water (Caspian Sea, Sari, Iran).

The soil standard reference material (CRM-SA-C (sandy soil)) obtained from Environmental Express Company (Charleston, South Carolina) was digested in an 8 mL mixture of 5% aqua regia with the assistance of a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, and 8 min at 550 W, and the mixture was then vented for 8 min, and the residue from this digestion was then diluted with deionized water. Finally, this method was applied for determination of lead from the aforementioned water samples. Soil samples were

TABLE 1: Optimization of the electrode composition.

Electrode no.	Graphite powder (%)	Paraffin (%)	Di-pyridile amine	Unmodified MWCNTs (%)	Modified MWCNTs (%)	Slope (mV)	Linear range (mol L ⁻¹)	R ²
1	75	25	0	0	0	11.9 ± 3.1	—	—
2	73	24	3	0	0	15.6 ± 2.2	3.5 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.915
3	72	23	5	0	0	19.3 ± 1.9	1.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.935
4	71	22	7	0	0	18.5 ± 1.9	1.5 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.928
5	73	24	0	3	0	13.5 ± 2.1	5.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.905
6	72	23	0	5	0	16.9 ± 1.8	2.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.919
7	70	23	0	7	0	20.2 ± 1.7	8.0 × 10 ⁻⁷ to 5.0 × 10 ⁻³	0.946
8	68	23	0	9	0	18.8 ± 1.9	1.5 × 10 ⁻⁶ to 1.0 × 10 ⁻²	0.939
9	72	23	5	5	0	25.0 ± 1.7	3.5 × 10 ⁻⁷ to 2.5 × 10 ⁻³	0.975
10	67	23	5	7	0	28.9 ± 1.1	7.5 × 10 ⁻⁸ to 2.5 × 10 ⁻³	0.995
11	65	23	5	9	0	27.8 ± 1.5	1.5 × 10 ⁻⁷ to 2.5 × 10 ⁻³	0.979
12	73	24	0	0	3	24.7 ± 1.7	5.0 × 10 ⁻⁷ to 2.5 × 10 ⁻³	0.966
13	72	23	0	0	5	26.3 ± 1.5	2.0 × 10 ⁻⁷ to 2.5 × 10 ⁻³	0.970
14	70	23	0	0	7	28.6 ± 1.2	9.5 × 10 ⁻⁸ to 2.5 × 10 ⁻³	0.990
15	67	23	0	0	9	28.0 ± 1.3	1.0 × 10 ⁻⁷ to 2.5 × 10 ⁻³	0.982

also collected randomly from a depth of approximately 1 cm in different place in Tehran, Iran.

NIST 1572 (*Citrus leaves*) standard reference material was obtained from National Institute of Standards and Technology (USA). In order to digest these leaves, after washing with distilled water, 1.0 g of it was grounded and dried out at 80 °C and triturated in a porcelain mortar. After sieving, the particles with sizes less than 20 μm were dissolve in 1 mL of 3 mol L⁻¹ HNO₃ solution and diluted with distilled water to 10 mL. The leaf sampling was carried out in spring of 2012 from Cedrus trees in different places in Tehran, Iran.

3. Results and Discussion

The response of a potentiometric carbon paste electrode is affected by conductivity of the electrode and selectivity of the chelating agent to the analyte. The conductivity can be improved by adding conductive materials like MWCNTs. Choosing a selective chelating agent like dipyrindile amine can improve the electrode selectivity, respecting adsorption of soft acid Pb²⁺ ion and soft base of dipyrindile amine. The lifetime of paste electrode is affected by stability of the electrode composition. By stabilizing dipyrindile amine on the surface of MWCNTs, the lifetime of the electrode was improved.

3.1. Dipyrindile Amine Functionalized Multiwalled Carbon Nanotube Characterization. A schematic diagram of this synthesis is represented in Figure 1. The formation of dipyrindile amine functionalized multiwalled carbon nanotube was confirmed by IR spectroscopy, elemental analysis, SEM micrograph, and thermal analysis. IR (KBr, cm⁻¹): 3440 (NH), 3037 (CH, aromatic), 2983 (CH, aliphatic), 1653 (C=N pyridine), 1607 (C=C pyridine), 890 (MWCNT).

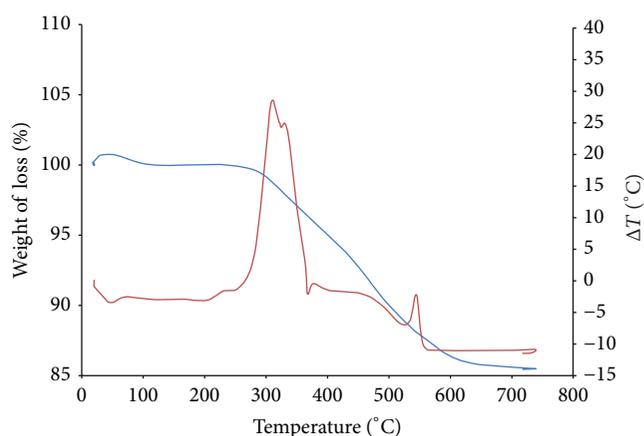


FIGURE 2: TG-DTA diagram of dipyrindile amine MWCNT.

According to elemental analysis results (C, 9.42; H, 0.81; N, 3.31%), the dipyrindile amine concentration on the surface of this sorbent is 136 mg g⁻¹. The thermal analysis of this composite confirmed the elemental analysis results as there is approximately 13% weight reduction in TG curve. Also the DTA curve showed that this composite is stable up to 230 °C (Figure 2). Finally, the SEM micrograph of this composite shows the nanostructure of dipyrindile amine functionalized multiwalled carbon nanotube (Figure 3).

3.2. Electrode Composition. Since the electrode composition is the most important factor in the responses and selectivity of the electrode, different amounts of graphite powder, paraffin oil, unmodified MWCNTs, dipyrindile amine, and modified MWCNTs were thoroughly mixed, and the responses were studied and listed in Table 1. In the first study no MWCNTs

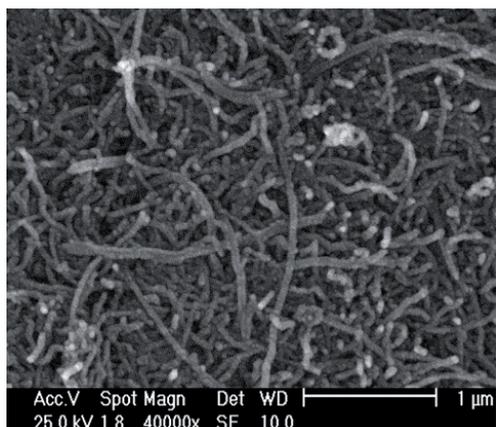


FIGURE 3: SEM micrograph of dipyrindile amine MWCNT.

and dipyrindile amine were added to the electrode (electrode no. 1). Then some amounts of dipyrindile amine were added to the electrode, and interaction of dipyrindile amine with lead ions improved the electrode performance (electrode no. 2–4). The influence of adding unmodified MWCNTs in the electrode performance was studied in electrode no. 5–8. In electrode no. 9–11, a mixture of dipyrindile amine and unmodified MWCNTs was used, and a Nernstian slope of 28.9 mV in a linear range of 7.5×10^{-8} to 2.5×10^{-3} mol L⁻¹ was observed in electrode no. 10. In electrode no. 12–15, modified MWCNTs were added to the electrode, and in electrode no. 14 a Nernstian slope of 28.6 mV in a linear range of 9.5×10^{-8} to 2.5×10^{-3} mol L⁻¹ was observed. In the next studies, electrode no. 14 with the composition of graphite powder 70%, paraffin 23% and modified MWCNTs 7% (W/W) was chosen as the optimum composition and its performance was compared to the electrodes no. 10 with the composition of graphite powder 67%, paraffin 23%, dipyrindile amine 5%, and unmodified MWCNTs 7% (W/W).

3.3. Calibration Curve. For quantitative determination of Pb(II) ions, a calibration curve in the linear range of 9.5×10^{-8} to 2.5×10^{-3} mol L⁻¹ was drawn versus measurements of Emf by electrode no. 14. The standard deviation for ten replicates is 1.2 mV. Results were shown in Figure 4. By extrapolating the linear parts of the ion selective calibration curve, the detection limit of the electrode was calculated to be 7.0×10^{-8} mol L⁻¹ [1, 27].

3.4. Influences of pH. For investigation of pH independent range of electrode no. 14, its potential response at concentration of Pb(II) ion (1.0×10^{-5} M) in a wide pH range (2.0–9.0) was measured. Various pH adjustments were done using concentrated HNO₃ or NaOH. The potential response as a function of pH value is depicted in Figure 5. As it is seen, the potential response of the Pb(II) electrode is almost constant between pH (5–7), and in this pH range, no interference from H₃O⁺ in acidic pH or OH⁻ in basic pH is observed. The pH = 6 was chosen as the optimum pH for all measurements. The effect of pH on electrode no. 10 was similar to electrode

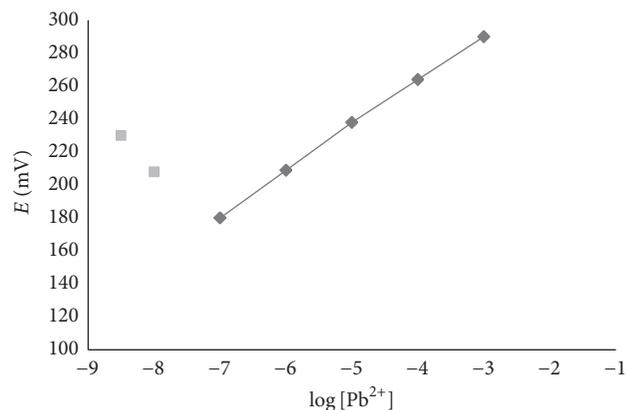


FIGURE 4: The calibration curve for Pb(II) ion, pH = 6.

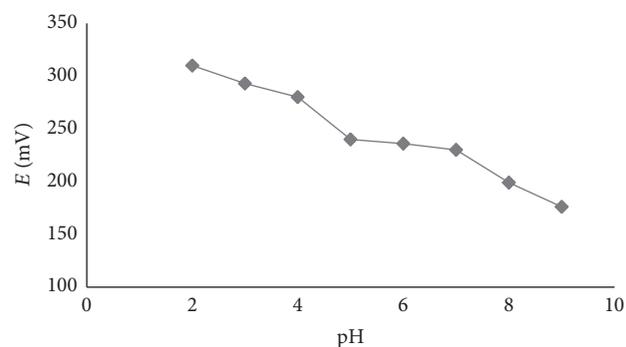


FIGURE 5: Influence of pH on electrode response to lead(II).

TABLE 2: Matched potential selectivity coefficient for interfering cations.

Interfering ions (X)	k_{Hg-X}^{MPM}
Na ⁺	2.1×10^{-4}
K ⁺	8.4×10^{-4}
Cs ⁺	3.1×10^{-3}
Ca ²⁺	6.3×10^{-4}
Mg ²⁺	7.7×10^{-4}
Cd ²⁺	4.3×10^{-3}
Ni ²⁺	8.1×10^{-3}
Cu ²⁺	2.9×10^{-3}
Cr ³⁺	7.4×10^{-3}
Fe ³⁺	4.5×10^{-3}
Ag ⁺	7.8×10^{-3}
Zn ²⁺	8.3×10^{-3}

no. 14 which should be related to presence of dipyrindile amine in the electrode composition.

3.5. Study of Response Time. The average static response time was defined as the required time for the sensors to reach a potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference [1, 27]. The Pb(II) concentration was changed in the liner range, and the results

TABLE 3: The lifetime of the electrode no. 14 and electrode no. 10. The results are based on triplicate measurements.

Week	Electrode no. 14		Electrode no. 10	
	Slope (mV)	Detection limit (mol L ⁻¹)	Slope (mV)	Detection limit (mol L ⁻¹)
First	28.6	7.0×10^{-8}	28.9	4.5×10^{-8}
Second	28.5	7.5×10^{-8}	28.0	8.9×10^{-8}
Third	28.3	8.1×10^{-8}	27.5	1.9×10^{-7}
Fourth	28.0	9.6×10^{-8}	25.1	5.9×10^{-7}
Fifth	27.7	2.0×10^{-7}	16.2	—
Sixth	27.1	5.1×10^{-7}	—	—
Seventh	26.7	8.1×10^{-7}	—	—
Eighth	26.1	8.9×10^{-7}	—	—
Ninth	25.6	9.5×10^{-7}	—	—
Tenth	25.2	1.3×10^{-6}	—	—
Eleventh	22.1	—	—	—

TABLE 4: Recovery of determination of Pb(II) ions in certified reference materials.

Sample	Unit	Concentration		Added	Found	Recovery (%)
		Certified	Found			
ERM-CA022 (drinking water)	$\mu\text{g L}^{-1}$	26 ± 0.9	24.9	—	—	95.8
CRM-SA-C (sandy soil)	mg kg^{-1}	133.0 ± 0.6	128.3	—	—	96.4
NIST 1572 (citrus leaves)	mg kg^{-1}	13.3 ± 2.4	13.1	—	—	98.4
Tap water	$\mu\text{g Kg}^{-1}$	ND	ND	20.0	19.9	99.7
Distilled water	$\mu\text{g Kg}^{-1}$	ND	ND	20.0	19.8	99.4
Sea water	$\mu\text{g Kg}^{-1}$	ND	ND	20.0	19.6	98.3
North soil	$\mu\text{g Kg}^{-1}$	47.1^a	46.2	20.0	63.7	96.2
South soil	$\mu\text{g Kg}^{-1}$	64.7^a	64.2	20.0	81.8	97.1
North leaves	$\mu\text{g Kg}^{-1}$	27.4^a	27.2	20.0	46.6	98.6
South leaves	$\mu\text{g Kg}^{-1}$	31.9^a	31.8	20.0	51.1	98.5

^aCertified by previously established method [1].

were studied. The results showed that the response time for the proposed electrode is 50 seconds. The same procedure was performed with electrode no. 10, and the response time was evaluated to be 3 minutes. The fast response time of electrode no. 14 might be as a result of presence of dipyrindile on the surface of MWCNTs.

3.6. Influence of Interference Ions. Matched potential method (MPM) is the recommended method for studying influence of interferences ions in ion selective electrodes by IUPAC [28]. The method is based on measuring the specific activity of the primary ion which is added to a reference solution. In this study the interfering ions were successively added to an identical reference solution with concentration of $5.0 \times 10^{-7} \text{ mol L}^{-1}$, until the measured potential matched to obtained value before adding the primary ions. Then matched potential selectivity coefficient, $k_{\text{pb},X}^{\text{MPM}}$, is calculated from the resulting primary ion to the interfering ion activity ratio, $k_{\text{pb},X}^{\text{MPM}} = \Delta(a_{\text{Hg}}/a_x)$ [29]. The interference of Na^+ , K^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Cr^{3+} , Fe^{3+} , Ag^+ , and Zn^{2+} was investigated and showed that they have no significant effect on the response to Pb^{2+} . The $k_{\text{pb},X}^{\text{MPM}}$ values for the interferences are shown in Table 2. The effect of interference ions on

electrode no. 10 was also studied, and similar selectivity to electrode no. 14 was observed which should be related to selectivity of dipyrindile amine with lead ions.

3.7. Lifetime. The lifetime of an electrode is the period of time that the electrode shows no changes in the efficiency of the measurements. To study this factor, the electrode was calibrated periodically with standard lead solutions. Then the electrode was conditioned and calibrated in the next week. As the results in Table 3 show, the lifetime of the electrode was evaluated to be ten weeks. The lifetime of the electrode no. 10 was evaluated to be four weeks. The long lifetime period of electrode no. 14 may be due to stability of dipyrindile amine on the surface of MWCNTs.

3.8. Method Validation. Different type of standard reference materials (water, soil, and plant) was used for validation of this method. The samples were digested by mentioned method, and the Pb(II) contents were analysed by this method. As it can be seen in Table 4, the results have good compatibility with certified ones. Moreover after validation of method by standard references materials, this method was applied for determination of Pb(II) concentrations in different environmental samples, and the results were compared to

previously established method for determination of lead ions by inductive coupled plasma spectroscopy reported by Li et al. [30]. Being accurate and precise, this method could be a sensitive and confidence method for determination of lead in various environmental samples such as soil, water, and plants.

4. Conclusion

Two carbon paste electrodes were developed for determination of lead ions. In one electrode the performance of the electrode was improved by adding MWCNTs and dipyrindile amine. In the other electrode dipyrindile was chemically modified on the surface of MWCNTs and added to the electrode as a modifier, and the performance of the second electrode was improved in terms of response time and lifetime. Method validation was done by analysis of standard reference materials with a matrix of water, soil, and plant.

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