Potentiometric Determination of Aluminum in Foods, Pharmaceuticals, and Alloys by AlMCM-41-Modified Carbon Paste Electrode

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Abstract A new chemically modified electrode is constructed by incorporating AlMCM-41 into carbon paste matrix (AlMCM-41-MCPE) and used as a sensitive sensor for detection of aluminum in aqueous and nonaqueous solutions. The rapid exchange kinetics in the membrane results in a near-Nernstian behavior of the modified electrode and makes it a suitable potentiometric sensor for detection of aluminum. A linear response in concentration range from 1.0×10^{-6} to 1.0×10^{-1} mol/L (0.027 μg/mL–2.7 mg/mL) was obtained with a detection limit of 4.6×10^{-7} mol/L for the potentiometric detection of aluminum. Selectivity coefficients of a number of interfering cations have been estimated. The interference from many of the investigated ions is negligible. The AlMCM-41-MCPE is suitable for use in aqueous solution of pH 2–6 and in partially nonaqueous medium. The modified electrode exhibited a fast response time (~8 s), good stability, and an extended lifetime. The developed sensor was used successfully for the determination of Al^{3+} in some alloys, drugs, and food products.

Keywords Aluminum · Modified carbon paste electrode · AlMCM-41 · Food products · Potentiometry

Introduction

During the last two decades, many studies have focused on the toxicity of aluminum on living systems, especially on human being, and it is believed that aluminum plays important roles in the pathology of Parkinson's disease,

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Alzheimer's disease, and diseases of dialysis (Paik et al. 1997). In this concern, nonelectrochemical techniques were used to measure aluminum including spectrophotometry (Tontrong et al. 2012; Francisco et al. 2010; Bulut et al. 2010; Abbasi et al. 2009; Huseyinli et al. 2009; Shokrollahi et al. 2008; Zheng et al. 2007; Bahram et al. 2007; Guray et al. 2005; Madrakian et al. 2005), spectrofluorimetry (Khan et al. 2011; Kara et al. 2008; Buratti et al. 2006; Beniz Gündüza et al. 2005; Zhu et al. 2004), acoustic wave sensor (Verissimo and Gomes 2008), electrothermal atomic absorption spectrometry (ETAAS) (Komárek et al. 2007; Burguera et al. 2005), graphite furnace atomic absorption spectrometry (GFAAS) (Sun and Wu 2010; Safavi et al. 2009; Tuzen and Soylak 2008; Sang et al. 2008; Tria et al. 2007; Narin et al. 2004), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Tria et al. 2007; Ščančar et al. 2004), inductively coupled plasma mass spectrometry (ICP-MS) (Tria et al. 2007; Xia et al. 2005), inductively coupled plasma optical emission spectrometry (ICP-OES) (Rezaee et al. 2010; Pacheco et al. 2008), chemiluminescence (Nie and Lu 2008; Shen and Fang 2008), diffuse reflectance spectroscopy (Zanjanchi et al. 2006), electron capture detection-gas chromatography (Measures and Edmond 1989), and RP-HPLC (Lian et al. 2004). A number of electrochemical techniques have been also developed to measure aluminum such as voltammetry (Di et al. 2004), stripping voltammetry (Arancibia and Muñoz 2007; Tria et al. 2007; Kefala et al. 2006; Qiong et al. 2006), and potentiometry (Arvand et al. 2010; Gupta et al. 2007; Mousavi et al. 2001; Abbaspour et al. 2002; Arvand and Asadollahzadeh 2008; Gupta et al. 2009; Saleh et al. 2001; Evsevleev et al. 2005; Yari et al. 2006).

Carbon pastes are well-known as useful materials for the fabrication of various electrochemical sensors for analytical purposes (Yeom et al. 1999; Abbas and Mostafa 2003). The operation mechanism of such chemically modified carbon

paste electrodes (CMCPEs) depends on the properties of the modifier materials used to import selectivity towards the target species (Abbas and Mostafa 2003). CMCPEs have generated great interest in recent years, especially in the fields of electroanalysis, due to being well-recognized as more advantageous than conventional electrodes (Kalcher et al. 1995). This continuous interest in CMCPEs has increased to use of inorganic materials as electrode modifier agents (Walcarius 1999).

MCM-41 molecular sieves are a new class of mesoporous aluminosilicates, the synthesis of which was first reported by researchers of the Mobil Oil Corporation (Kresge et al. 1992; Beck et al. 1992). They are prepared by hydrothermal precipitation of amorphous silica alumina in the presence of quaternary ammonium surfactants and display cylindrical regular mesopores of monodispersed diameters from 1.5 to 10 nm with potential applications in catalysis and adsorption. Pure silica MCM-41 s, with better stability as compared to their silica-alumina analogues, have also been prepared. These solids feature very high surface areas (up to about 1,000 m^2/g) and their internal surfaces present silanol moieties located at defect sites ($\equiv$SiOH$\cdots$HOSi$\equiv$), due to the interruption of Si–O–Si linkages (Weglarski et al. 1996). The silanol groups situated on the mesoporous surface of the MCM-41-type silica are the same as those of the traditional amorphous silica (Brunel et al. 1995) and the number of internal $\equiv$SiOH groups (with some $=$Si(OH)$_2$ groups) is quite large, due to a low degree of connectivity in mesoporous materials (Kolodziejski et al. 1993). The reaction of these hydroxyl groups with various alkoxysilanes has recently been exploited for preparing functionalized MCM-41 by covalent grafting with various organic moieties (Brunel et al. 1995; Mercier and Pinnavaia 1997; Díaz et al. 1997).

The unusual properties of mesoporous aluminosilicates have attracted increasing attention in electroanalytical chemistry. In particular, the unique molecular sieving, cation exchange, and electrocatalytic properties of these compounds have led to several interesting electroanalytical applications (Walcarius et al. 1998). MCM-41 has been investigated extensively because the other materials in this family are either thermally unstable or are difficult to obtain (Zanjanchi and Asgari 2004). The purpose of this communication is to investigate the construction, potentiometric characterization, and analytical application of a modified carbon paste electrode selective for aluminum based on the use of AlMCM-41.

Materials and Methods

Reagents

All chemicals used were of analytical reagent grade unless otherwise stated. Paraffin oil, aluminum nitrate, graphite powder (particle size <50 μm), hydrochloric acid (HCl), ethanol, acetone, acetonitrile, and chloride or nitrate salts of other cations were all obtained from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland) and used without further purification. Doubly distilled, deionized water was used for preparing all of the solutions.

Apparatus and Emf Measurements

Potentiometric measurements were carried out with the following cell assembly: AlMCM-41-MCPE | test solution | Ag-AgCl, KCl (sat'd). The cell consists of AlMCM-41-MCPE as the indicator electrode, a saturated Ag-AgCl reference electrode, and a magnetic stirrer. A digital pH/millivoltmeter (Jenway, Model 3305) at laboratory was used for measuring potentials. A digital pH meter (Metrohm 827) was used for measuring pH. The reference electrode was obtained from Azar Electrode Company (Urmia, Iran).
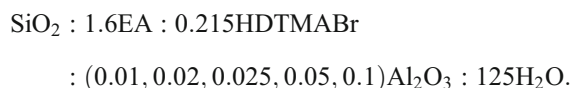
Preparation of AlMCM-41

The purely siliceous parent MCM-41 was synthesized by a room temperature synthesis method with some modification in the described procedure from the literature (Zanjanchi and Asgari 2004). We used tetraethylorthosilicate (TEOS) as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr, BDH, Poole, England) as template for preparation of MCM-41 materials. The procedure for MCM-41 synthesis is as follows: 2.7 g ethylamine (EA) was added to 42 mL of deionized water and the mixture was stirred at room temperature for 10 min. The amount, 1.47 g, of the surfactant (HDTMABr) was gradually added to the above solution under stirring for 30 min. After further stirring for 30 min, a clear solution was obtained. Then, 2.1 g of TEOS solution was added dropwisely to the solution. The molar composition of the mixture was:

$$SiO_2 : 1.6\,EA : 0.215\,HDTMABr : 125\,H_2O.$$

The pH of the reaction mixture was adjusted to 8.5 by slow addition of HCl solution (1.0 mol/L) to the mixture. At this stage, the precipitate is formed. After 2 h, under slow stirring, the precipitate was separated and washed by centrifugation. The sample was dried at 45 °C for 12 h.

The MCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain white powder. This powder was used as the parent material to prepare AlMCM-41 materials by postsynthesis alumination method. For this modification, 1.0 g of calcined siliceous MCM-41 was treated in aqueous aluminum sulfate solution with different concentrations. This mixture is stirred for 2 h and left at room temperature for 48 h. After recovering the solid by filtration and several washing steps with hot deionized water, the sample was dried at 45 °C for 12 h.

Five samples with different molar Si/Al ratios, containing the same amounts of aluminum as those prepared by post-synthesis method, are obtained by a direct (isomorphous substitution) synthesis method. The procedure is similar to the method described above for siliceous MCM-41 but with the addition of aluminum sulfate to the mixture before pH adjustment. The final molar composition of the reacting mixture was as follows:

$$SiO_2 : 1.6EA : 0.215HDTMABr$$

$$: (0.01, 0.02, 0.025, 0.05, 0.1)Al_2O_3 : 125H_2O.$$

Preparation of AlMCM-41-Modified Carbon Paste Electrode (AlMCM-41-MCPE)

The general procedure to prepare the modified carbon paste electrode was to mix graphite powder with AlMCM-41 (Si/Al=5) (3 % w/w) and mineral oil (paraffin oil, 30 % w/w). After thorough hand mixing in a mortar and pestle to obtain a very fine paste, a portion of the composite mixture was packed into the end of a Pyrex glass tube (ca. 3 mm i.d. and 10 cm long). Electrical contact was made by forcing a copper wire down the glass tube and into the back of the mixture. The working surface of the electrode was polished using a soft polishing tissue to obtain a shiny surface. The indicator electrode was conditioned by soaking in a 1×10^{-2} mol/L aqueous aluminum solution for 10 h.

Sample Preparation and Determination

Tap water, mushroom, tomato sauce, multivitamin capsule, rice, black tea, potato, and some alloys were selected for analysis. Potato, mushroom, and rice were obtained from Iranian agricultural farms and tea was brought in a tea shop.

Determination of Aluminum in Rice

Ten grams of ground rice sample was accurately weighed and placed into a quartz crucible. Ten milliliters of concentrated sulfuric acid was added to it and evaporated to near dryness; then, 10 mL of nitric acid (1+1, volume ratio) was added and evaporated to dryness. Under the heating conditions, concentrated hydrogen peroxide was added by drop till the solution cleared and evaporated. Water was added and was heated continuously to remove the hydrogen peroxide. The residue cooled and was transferred into a 200-mL calibrated flask and diluted to the mark with water. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions. The results are presented in Table 6.

Determination of Aluminum in Tea

Tea sample (3.9883 g) was accurately weighed and placed into a ceramic crucible. Six milliliters of concentrated nitric acid and 2 mL of concentrated HCl were added. After 20 min, the sample was gently heated to digest till near dryness. It is transferred into muffle furnace for ashing at 600 °C for 1 h. The sample was taken out to cool and 5 mL of nitric acid (1+1, volume ratio) was added and evaporated to near dryness by gentle fire heating. Two grams of ammonium peroxydisulfate was added to cover the residue. The sample was transferred to muffle furnace at 800 °C for ashing for 1 h. It cooled and was taken out. Ten milliliters of nitric acid (1+99, volume ratio) was used to dissolve the residue and transferred to a 100-mL calibrated flask and diluted to the mark with water. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum; the results are presented in Table 6.

Determination of Aluminum in Potato and Mushroom

The potato and mushroom samples were washed and cut into bars. Then, the samples were dried at 110 °C for 4 h. Ten grams of the dried samples was accurately weighed and placed into a ceramic crucible. The samples were put into muffle furnace for ashing at 650 °C for 8 h. After the ashing was completed, the furnace was opened and the samples cooled and were taken out. After the samples cooled to room temperature, a few drops of water were added and 5 mL of HCl (1+1, volume ratio) was added to dissolve the residues. The above substances were transferred to a 50-mL calibrated flask and diluted to the mark with water. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions. The results are presented in Table 6.

Determination of Aluminum in a Multivitamin Capsule

Three grams of multivitamin syrup was accurately weighed and placed into a ceramic crucible. Five milliliters of concentrated nitric acid was added to it and evaporated to near dryness; then, 10 mL of water was added and evaporated to dryness. The residue cooled and 50 mL of water was added to dissolve the residue and transferred to a 500-mL calibrated flask and diluted to the mark with water. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum; the results are presented in Table 6.

Determination of Aluminum in Tomato Sauce

Five grams of tomato sauce sample was accurately weighed and placed into a quartz crucible. The sample was put into

Table 1 Percentage content of each alloy

Alloy	Percentage content of the alloy (%)					
	Fe	Cu	Zn	Pb	Ni	Al
Magnesium-based alloy NBS171	0.0018	0.011	1.05	0.003	0.001	2.98
Copper-based alloy NBS164	2.52	63.76	21.89	0.22	0.046	6.21
Zinc-based alloy NIST 94C	0.018	1.01	94.83	0.018	0.006	4.13

muffle furnace for ashing at 550 °C for 90 min. After the ashing was completed, the furnace was opened and the sample cooled and was taken out. After the sample cooled to room temperature, 10 mL of concentrated nitric acid was added to dissolve the residue and evaporated to dryness. Water was added and heated continuously to remove the excess nitric acid. This work was repeated three times. Finally, the residue was cooled and dissolved into 50 mL of water and transferred to a 250-mL calibrated flask and diluted to the mark with water. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions. The results are presented in Table 6.

Determination of Aluminum in Some Alloys

According to Table 1, percentage content of each alloys was accurately weighed and completely dissolved in 20–40 mL of HCl on a water bath and then 2–3 mL of 30 % hydrogen peroxide was added. The excess of peroxide was decomposed by heating the solution on a water bath and the mixture was cooled and filtered through a filter paper (Whatman No. 1). The filtrated mixture was diluted to 500 mL with distilled water in a calibrated flask. Volumes of 10 mL of each of the aliquots were taken for the determination of aluminum via the recommended procedure under the established optimum conditions. The results are presented in Table 7.

Results and Discussion

Influence of the Electrode Composition

We started our preliminary works on five AlMCM-41 zeolites with different Si/Al ratios as indicated below:

$$AlMCM - 41(5), AlMCM - 41(10), AlMCM$$
$$- 41(20), AlMCM - 41(25), AlMCM - 41(50).$$

We have examined these to find out the best one to give near-Nernstian response to Al^{3+} ions. Our preliminary experiments showed that the carbon paste sensor prepared by using AlMCM-41 zeolite with Si/Al ratio of 5 as ion sensing proved to be a suitable one. In fact, AlMCM-41 (5) has much higher concentrations of exchangeable sites compared to those of AlMCM-41 (10), AlMCM-41 (20), AlMCM-41 (25), and AlMCM-41 (50). This certainly will affect the performance of the membrane as its mechanism is based on ion exchange property.

As mentioned above, the carbon paste sensors are based on the ion exchange mechanism of the active component incorporated into the carbon paste matrix. In context, the pore size and exchange capacity of zeolite can affect the functioning of the electrode. On the other hand, MCM-41 is a mesoporous aluminosilicate with relatively very large pores. This pore size will let large cations such as Al^{3+} to enter to the space inside of the mesoporous aluminosilicate for exchange. Thus this is not an effective factor for the response of the proposed electrode. In addition, there is no significant difference between the pore aperture from the point of different Si/Al ratios (Table 2). The different responses (slope of the calibration plot) are really related to variation in the exchange capacity of the mesoporous compound. The variation is caused by the change of Si to Al ratios in the mesoporous MCM-41. Thus, we could deduce that the exchange capacity of the zeolite is important for proper functioning of the proposed electrode. According to this point, MCM-41 with Si/Al ratio of 5 has much higher concentrations of exchangeable sites and it is expected to respond to Al^{3+} ions with better sensitivity. Therefore, all of working conditions were done on AlMCM-41 (5)-MCPE.

It is well-established that the sensitivity, linearity, and selectivity of the ion exchange-based electrodes depend significantly on the membrane composition. Thus, the influence of the percent of AlMCM-41 in the carbon paste composition was investigated and the results are summarized in Table 3.

Table 2 Comparison of the behavior of different AlMCM-41-MCPEs with different pore sizes

Zeolite	Si/Al[a]	Pore size (A°)	Slope (mV/decade)
AlMCM-41 (5)	4.8	27.2	19.8±0.4
AlMCM-41 (10)	9.6	26.3	17.3±0.3
AlMCM-41 (20)	19.3	25.5	15.5±0.8
AlMCM-41 (25)	23.4	25.2	15.4±0.6
AlMCM-41 (50)	48.1	24.4	11.6±0.8

[a] Determined by ICP analysis

Table 3 Influence of the compositions of the AlMCM-41-MCPE on its general characteristics

AlMCM-41 (5) (%)	Slope (mV/decade)	LWR (mol/L)	LLOD (mol/L)
0	3.4 ± 0.6	1.0×10^{-2} to 1.0×10^{-5}	–
1	8.6 ± 1.0	1.0×10^{-2} to 1.0×10^{-6}	1.0×10^{-6}
2	14.2 ± 0.7	1.0×10^{-2} to 1.0×10^{-6}	2.3×10^{-7}
3	19.8 ± 0.4	1.0×10^{-1} to 1.0×10^{-6}	4.6×10^{-7}
5	17.5 ± 0.7	1.0×10^{-1} to 1.0×10^{-6}	1.0×10^{-6}
7	16.3 ± 0.8	1.0×10^{-1} to 1.0×10^{-6}	1.0×10^{-6}

LWR linear working range, *LLOD* lower limit of detection

For this purpose, five electrodes were prepared, in which the amounts of carbon powder and paraffin oil were kept constant. The proportions of modifier in these electrodes were 1, 2, 3, 5 and 7 % (w/w). It has been found that the electrode containing zero percentage of modifier showed a negligible response towards aluminum cations; however, increasing the amount of the modifier up to 3 % has led to a sharp increase of the electrode response. Much increase in the modifier percentage from 3 to 7 % has lead to a decrease again in the electrode response. This may be explained by the decrease in the conductance of the electrode material with increase of the percentage of the modifier. Thus, the electrode containing 3 % of the modifier was found to have a Nernstian slope and wide range of linearity, while electrodes containing a higher ratio of the modifier showed nonlinearly in their response. Therefore, 3 % of AlMCM-41 was chosen as the optimum amount of the modifier for preparing the purposed electrode.

Performance Characteristics of the Developed AlMCM-41-MCPE

The potentiometric response characteristics of the ion selective electrode based on the use of AlMCM-41 as a modifier in a graphite powder matrix were evaluated according to IUPAC recommendations (IUPAC Analytical Chemistry Division 1994). The AlMCM-41-MCPE displays a linear response from 1.0×10^{-1} to 1.0×10^{-6} mol/L aluminum with a Nernstian cationic slope of 19.8 ± 0.4 mV per concentration decade with the detection limit of 4.6×10^{-7} mol/L. The least squares equation obtained from the calibration data is E (mV)=(19.8 ± 0.4) log $[Al^{3+}]+(203.6\pm0.7)$. The results are summarized in Table 4 and compared with the results of recently reported modified electrodes, which have been used for the determination of aluminum. As shown in this table, the performance of the proposed electrode is almost comparable with these modified electrodes. Although there are some modified electrodes that may be more superior than our electrode, our comparison is meant to illustrate that, despite its simplicity, the proposed electrode can also compete with these electrodes.

Effect of pH on the Response of the AlMCM-41-MCPE

The electrode response for different aluminum concentrations was tested over the pH range of 1.0–7.0; pH was adjusted using HCl. The AlMCM-41-MCPE has been successively dipped into aluminum nitrate solution of 1×10^{-4} and 1×10^{-5} mol/L, and the resulting potential of the electrode after being stable was plotted against the

Table 4 Comparison of the AlMCM-41-MCPE with some recently reported modified electrodes for aluminum detection
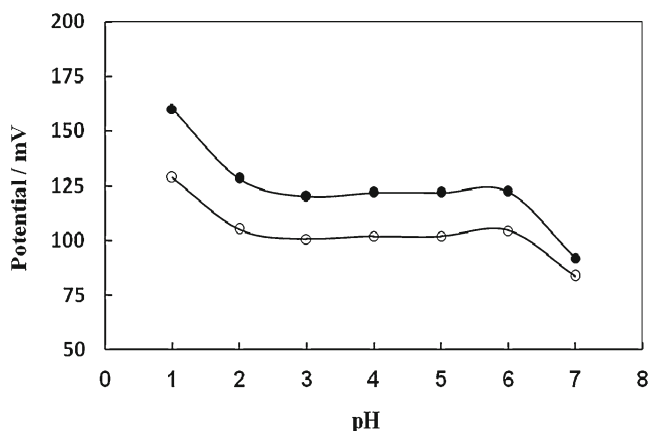
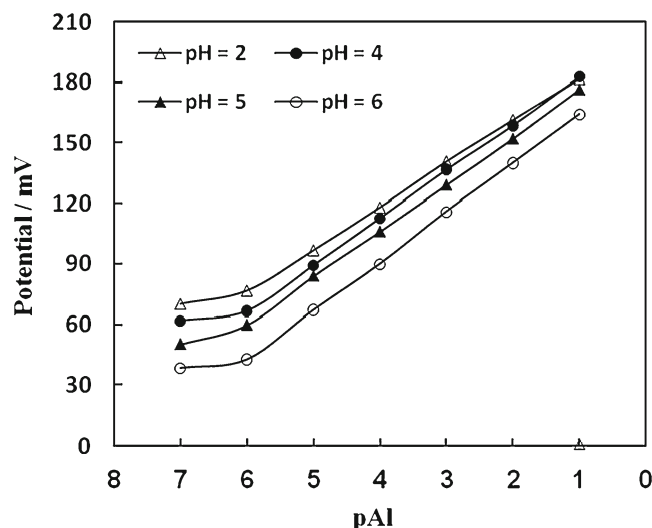| Ionophore	Slope (mV/decade)	pH range	Lifetime	Detection limit (mol/L)	Linear range (mol/L)	Ref.
Bis(5-phenylazo salicylaldehyde) 2,3-naphthalene diimine	19.3 ± 0.8	3.5–5.0	>2 months	2.5×10^{-6}	5.0×10^{-6}–1.0×10^{-2}	Abbaspour et al. (2002)
7-Ethylthio-4-oxa-3-phenyl-2-thioxa-1,2-dihydro-pyrimido [4,5-d]pyrimidine	19.5	2.25–3.25	1 month	3.2×10^{-6}	1.0×10^{-5}–1.0×10^{-1}	Saleh et al. (2001)
Aluminon	29.5	–	2 months	1.0×10^{-6}	1.0×10^{-5}–1.0	Babenikov et al. (2005)
Zeolite-based PVC membrane	19.5 ± 0.4	3–6	3 months	8.6×10^{-8}	1.0×10^{-7}–1.0×10^{-1}	Arvand et al. (2010)
1-Hydroxy-3-methyl-9-xanthen-9-one	20.0 ± 0.2	3–8.5	3 months	6.0×10^{-7}	1.6×10^{-6}–1.0×10^{-1}	Yari et al. (2006)
N,N'-bis(salicylidene)-1,2-cyclohexanediamine (NBSC)	20.3 ± 0.1	2.0–9.0	3 months	5.0×10^{-9}	1.0×10^{-8}–1.0×10^{-1}	Gupta et al. (2009)
6-(4-Nitrophenyl)-2-phenyl-4-(thiophen-2-yl)-3,5-diaza-bicyclo[3.1.0]hex-2-ene	19.6 ± 0.4	3–6	>3 months	6.3×10^{-7}	1.0×10^{-6}–1.0×10^{-1}	Arvand and Asadollahzadeh (2008)
Furil	18.5 ± 0.7	0.5–3.0	2 months	1.3×10^{-7}	1.0×10^{-6}–1.0×10^{-2}	Mousavi et al. (2001)
Morin	19.7 ± 0.1	3.5–5	2 months	3.2×10^{-7}	5.0×10^{-7}–1.0×10^{-1}	Gupta et al. (2007)
AlMCM-41	19.8 ± 0.4	2–6	>4 months	4.6×10^{-7}	1.0×10^{-6}–1.0×10^{-1}	This work

pH of solution (Fig. 1). This figure shows that the potential is constant in the pH range 2.0–6.0. At pH values lower than 2.0, the pH of solution also affected the potential response. This is probably due to partial destruction of zeolite lattice, which occurs in acidic media (Breck 1974), and also to simultaneous response of the electrode to positively charged H_3O^+ and Al^{3+} ions. At higher pH, the formation of some hydroxyl complexes of Al^{3+} ions may be responsible for a decrease in potential responses. The calibration plots of potential of the modified electrode vs. logarithm of aluminum concentration at pH 2.0–6.0 were also investigated and the results are shown in Fig. 2. This figure shows that the slope per concentration decade is constant approximately (19.3 ± 0.7 mV/decade) in the pH range 2.0–6.0.

Response Time and Reversibility

The average time required for the Al^{+3} ion sensor to reach a potential within ± 1 mV of the final equilibrium value after immersion in a solution of Al^{+3} ion was measured. The static response time of the membrane sensor thus obtained was ~8 s for the concentration 1×10^{-4} mol/L, and potential stayed constant for more than 10 min after which only a very slow divergence within the resolution of the pH/mV meter (i.e., 0.1 mV) was observed (Fig. 3). Day-to-day reproducibility of the AlMCM-41-MCPE is about ± 0.5 mV for the same solution and the useful lifetime of the sensor is 6 weeks, during which the potential slope is reproducible to within ± 3 mV per concentration decade. A fresh electrode surface was obtained by squeezing out a small amount of paste and scraping off the excess against a conventional paper and then polishing the electrode on a smooth filter paper until the surface had a shiny appearance.
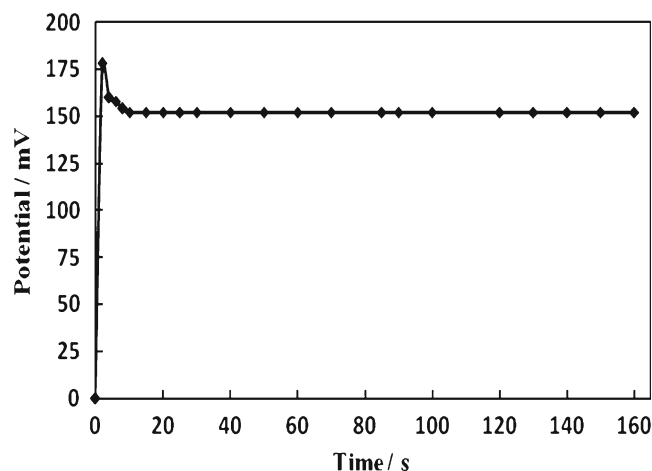

Fig. 2 Calibration plot of potential of AlMCM-41-MCPE vs. logarithm of aluminum ion concentration at pH values of 6 (*unfilled circle*), 5 (*filled triangle*), 4 (*filled circle*), 2 (*unfilled triangle*)

To evaluate the reversibility of the AlMCM-41-MCPE, some measurements were performed in the sequence of low-to-high sample concentrations and vice versa. The results showed that the potentiometric responses of the sensor was reversible and had any memory effect, although the time needed to reach equilibrium values were longer than that of low-to-high sample concentration. Noteworthy, it is well-documented that in the case of high-to-low concentration, the time needed to attain a stable potential is some 100 times larger than that required for the case of low-to-high concentrations (for a ten times change in the cation concentration).

Solvent Effect

The real sample may contain nonaqueous content, so the performance of the AlMCM-41-MCPE was also investigated

Fig. 1 Effect of pH on the potential response of the AlMCM-41-MCPE at two different concentrations: (*filled circle*) 1×10^{-4} mol/L and (*unfilled circle*) 1×10^{-5} mol/L

Fig. 3 Static response time of the proposed AlMCM-41-MCPE towards Al^{3+} ions

Table 5 Performance of the AlMCM-41-MCPE in partially nonaqueous media

Nonaqueous content (%, v/v)	Working concentration range (mol/L)	Slope (mV/decade)
0	$1.0\times10^{-6}-1.0\times10^{-1}$	19.8 ± 0.4
Ethanol		
5	$1.0\times10^{-6}-1.0\times10^{-1}$	19.7 ± 0.3
10	$1.0\times10^{-6}-1.0\times10^{-1}$	19.7 ± 0.3
15	$1.0\times10^{-6}-1.0\times10^{-1}$	19.2 ± 0.4
20	$1.0\times10^{-6}-1.0\times10^{-1}$	18.8 ± 0.7
Acetone		
5	$1.0\times10^{-6}-1.0\times10^{-1}$	19.5 ± 0.5
10	$1.0\times10^{-6}-1.0\times10^{-1}$	19.7 ± 0.5
15	$1.0\times10^{-6}-1.0\times10^{-1}$	18.2 ± 0.6
20	$1.0\times10^{-6}-1.0\times10^{-1}$	17.6 ± 0.8
Acetonitrile		
5	$1.0\times10^{-6}-1.0\times10^{-1}$	18.2 ± 0.7
10	$1.0\times10^{-5}-1.0\times10^{-1}$	17.4 ± 0.8
15	$1.0\times10^{-5}-1.0\times10^{-1}$	13.5 ± 0.8
20	$1.0\times10^{-5}-1.0\times10^{-1}$	9.6 ± 1.0

in partially nonaqueous media using 5 to 20 % (v/v) nonaqueous content in ethanol–water, acetonitrile–water, and acetone–water mixtures. The investigation showed that the AlMCM-41-MCPE does not show appreciable change in working concentration range ($1.0\times10^{-6}-1.0\times10^{-1}$ mol/L) or slope (19.8 ± 0.4 mV/decade of activity) in the presence of ethanol and acetone having up to 20 % (v/v) nonaqueous content, while the slope for acetonitrile decreased (Table 5). Therefore, the electrode is not suitable for use in acetonitrile–water mixtures.

Selectivity of the AlMCM-41-MCPE

The influence of different ions on the response of the AlMCM-41-MCPE has been investigated. The selectivity
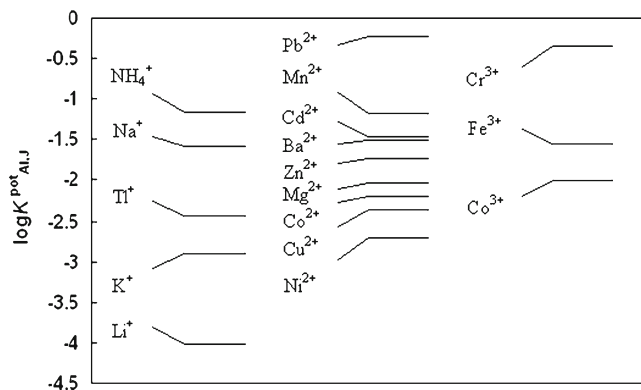
Fig. 4 Potentiometric selectivity coefficients of some common species, using the AlMCM-41-MCPE

Table 6 Determination of aluminum in some foods and drugs by direct potentiometry using the AlMCM-41-MCPE

Sample	Aluminum content (mg/g)[a]		t test[b]	F test
	Proposed method	AAS method		
Potato	0.18 ± 0.05	0.17 ± 0.03	0.3	2.8
Mushroom	0.20 ± 0.03	0.18 ± 0.05	0.59	2.8
Rice	0.14 ± 0.06	0.16 ± 0.06	0.41	1.0
Tea leave	0.38 ± 0.06	0.34 ± 0.03	1.03	4.0
Tomato sauce	1.08 ± 0.07	1.04 ± 0.04	0.86	3.1
Multi vitamin capsule	19.9 ± 1.2	22.0 ± 0.6	2.71	4.0

[a] $x = \overline{x} \pm s_x$ for $n=3$ and s_x denotes standard deviation

[b] The theoretical values of t and F at $P=0.05$ are 2.78 and 19.00, respectively

coefficients were determined by the separate solution method (SSM) (Hassan and Hamada 1988) using 1.0×10^{-3} mol/L concentration of both aluminum nitrate and the interfering species. The selectivity coefficient was calculated from the following equation:

$$\frac{E_1 - E_2}{S} = \log\left[a_{Al^{3+}}K^{Pot}_{Al^{3+},J}(a_J)^{\frac{1}{y}}\right] \tag{1}$$

where E_1 and E_2 are the potential readings observed after 1 min of exposing the sensor to the same concentration of aluminum ion and interfering ions alternatively, a_{Al} and a_J, the activities of the aluminum ion and interfering ions, y the charge of the interfering ion and S the slope of calibration graph (millivolt per concentration decade). Figure 4 reveals that the interference from almost all of the investigated ions is unimportant except Pb^{2+} and Cr^{3+}; this should be noticed during use of this electrode for real samples in presence of these ions.

Application

In order to investigate the applicability and selectivity of the proposed potentiometric method, the modified electrode

Table 7 Determination of aluminum in some alloys using the AlMCM-41-MCPE

Alloy	Aluminum found (%)[a]	
	Proposed method	AAS method
Magnesium-based alloy NBS171	2.97 ± 0.93	2.98 ± 0.71
Copper-based alloy NBS164	6.13 ± 0.48	6.21 ± 0.34
Zinc-based alloy NIST 94C	4.09 ± 1.05	4.13 ± 0.86

[a] Average of three determinations ± SD

was applied to the determination of aluminum in some alloys, drugs, and food product preparations using the standard addition method.

Determination of Aluminum in Drug and Food Products

The proposed electrode has been applied for the direct potentiometric determination of aluminum in tea leave, potato, mushroom, rice, multivitamin capsule, and tomato sauce. The pretreatment and determination procedures were the same as described in "Materials and Methods". For estimation of the validity of the proposed method, the determination of aluminum in samples was carried out by this method (pH 3.0) and atomic absorption spectrometry (AAS). The results are summarized in Table 6. As seen from Table 6, the results are in good agreement with those obtained by the AAS method. Thus, it can be concluded that the membrane electrode may have applications in the drug analysis and monitoring of Al^{3+} ions in food products. Moreover, due to its low detection limit and short response time, the proposed electrode can also be used as a suitable detector in flow injection analysis and ion chromatography monitoring of Al^{3+} ions.

Determination of Aluminum in Alloys

The AlMCM-41-MCPE has been examined for the determination of aluminum in alloys and the results are summarized in Table 7. The results show that the proposed method agreed well with the amount obtained by the standard method. Thus, it can be concluded that the membrane electrode may have applications in the industrial and environmental monitoring of Al^{3+} ions.

Conclusions

The sensitivity and stability offered by this simple electrode configuration are high enough to allow accurate determination of low levels of aluminum. The inherent advantages of the modified electrode are its simple operation, stability, precise results, low cost, and direct application to the determination of Al^{3+} ions, wide dynamic range, low detection limit, fast response time, and renewability of its surface by simple polishing, demonstrating its analytical utility as a sensor for determination of aluminum. The AlMCM-41-MCPE was successfully applied for the determination of Al^{3+} content in aqueous and nonaqueous solutions. It was successfully applied to the determination of Al^{3+} ions in various real samples.

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