Potentiometric sensor based on molecularly imprinted polymer for determination of melamine in milk

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ABSTRACT

A polymeric membrane ion-selective electrode for determination of melamine is described in this paper. It is based on a molecularly imprinted polymer (MIP) for selective recognition, which can be synthesized by using melamine as a template molecule, methacrylic acid as a functional monomer and ethylene glycol dimethacrylate as a cross-linking agent. The membrane electrode shows near-Nernstian response (54 mV/decade) to the protonated melamine over the concentration range of 5.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The electrode exhibits a short response time of ~16 s and can be stable for more than 2 months. Combined with flow analysis system, the potentiometric sensor has been successfully applied to the determination of melamine in milk samples. Interference from high concentrations of ions co-existing in milk samples such as K$^+$ and Na$^+$ can be effectively eliminated by on-line introduction of anion- and cation-exchanger tandem columns placed upstream, while melamine existing as neutral molecules in milk of pH 6.7 can flow through the ion-exchanger columns and be measured downstream by the proposed electrode in an acetate buffer solution of pH 3.7.

1. Introduction

Over the last few years, molecular imprinting technique has received considerable attention in the fields of polymer science and chemical analysis, owing to its predetermined selectivity for target molecular, high affinity and robustness [1,2]. Molecularly imprinted polymers (MIPs) are synthesized in the presence of functional monomers, template molecules and cross-linking agent by covalent [3], non-covalent [4] and sacrificial spacer methods [5]. Binding sites with molecular recognition properties are formed after template molecules are removed from the polymerized material, leaving behind cavities complementary in size and shape to the template for the subsequent rebinding process. MIPs have been extensively used in several applications such as solid phase extraction (SPE) [6], chromatographic separation [7], catalysis facilitation [8] and artificial reception [9].

In recent years, MIPs have been gained wide acceptance as new molecular recognition materials in chemical sensors, since they are more stable, less costly and easier to produce as com-

pared to their biological counterparts including antibodies and enzymes [10–12]. Various chemical sensors have been prepared using MIPs for molecular recognition followed by appropriate signal transductions including capacitance [13], conductometry [14], amperometry [15], voltammetry [16], quartz microbalance [17] and spectroscopy [18]. Potentiometric sensors are generic and highly successful approaches to chemical sensing, and MIP based potentiometric sensors have shown to be very promising [19]. Unlike sensors based other transduction techniques, potentiometric sensors do not require the template molecules to diffuse through the electrode membranes for generation of membrane potentials [19], thus dramatically reducing the response time. However, reports on MIP based potentiometric sensors are still rather rare [20–23].

Melamine, 1,3,5-triazine-2,4,6-triamine, slightly soluble in water, is a common organic compound that is often used with formaldehyde to produce melamine resin, a synthetic polymer as fire resistant and heat tolerant [24]. Melamine became a topic of much discussion in early 2007, when veterinary scientists determined it to be the cause of hundreds of pet deaths due to pet food contamination. Especially, the 2008 melamine-tainted-milk powder incident in China led to serious concern about melamine for food safety. Consequently, several methods have been developed for melamine detection in food, such as liquid chromatography coupled with mass spectrometry [25], solid phase extraction [26], ultraviolet spectrum, Raman spectroscopy and ion chromatogra-

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phy [27]. However, these methods require expensive apparatus and complicated pretreatment. Since potentiometric technique allows sensitive, simple and inexpensive detection of analyte, it would be a promising alternative for melamine analysis in food samples. In this paper, a polymeric membrane ion-selective electrode (ISE) based on MIP is described for the determination of melamine in milk. Melamine is a weak base with a pK_a of 5.05, and is readily protonated in aqueous solution at pHs lower than 5.0. The protonated melamine can thus be measured potentiometrically by the ISE. Interference from high concentrations of ions co-existing in milk such as K$^+$ and Na$^+$ can be effectively eliminated by on-line introduction of anion and cation-exchanger tandem columns placed upstream. To the best of our knowledge, this paper reports the first sensing system for rapid determination of melamine.

2. Experimental

2.1. Reagents and materials

Melamine, methacrylic acid (MAA), benzene and tetrahydrofuran (THF) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Ethylene glycol dimethacrylate (EGDMA), 2,2′-azobisisobutyronitrle (AIBN), 2-nitrophenyloctyl ether (NPOE), bis(2-ethylhexyl)sebacate (DOS), di-n-octyl phthalate (DOP), sodium tetrakis [3,5-bis(trifluoro-methyl)phenyl]borate (NaTFPB) and high molecular weight poly(vinyl chloride) (PVC) were purchased from Sigma-Aldrich. 732 strong-acid cation-exchange resin and 717 strong-base anion-exchange resin were obtained from Guoyao Chemical Reagent Co., Ltd. (Shanghai, China) for sample separation. Aqueous solutions were prepared with freshly
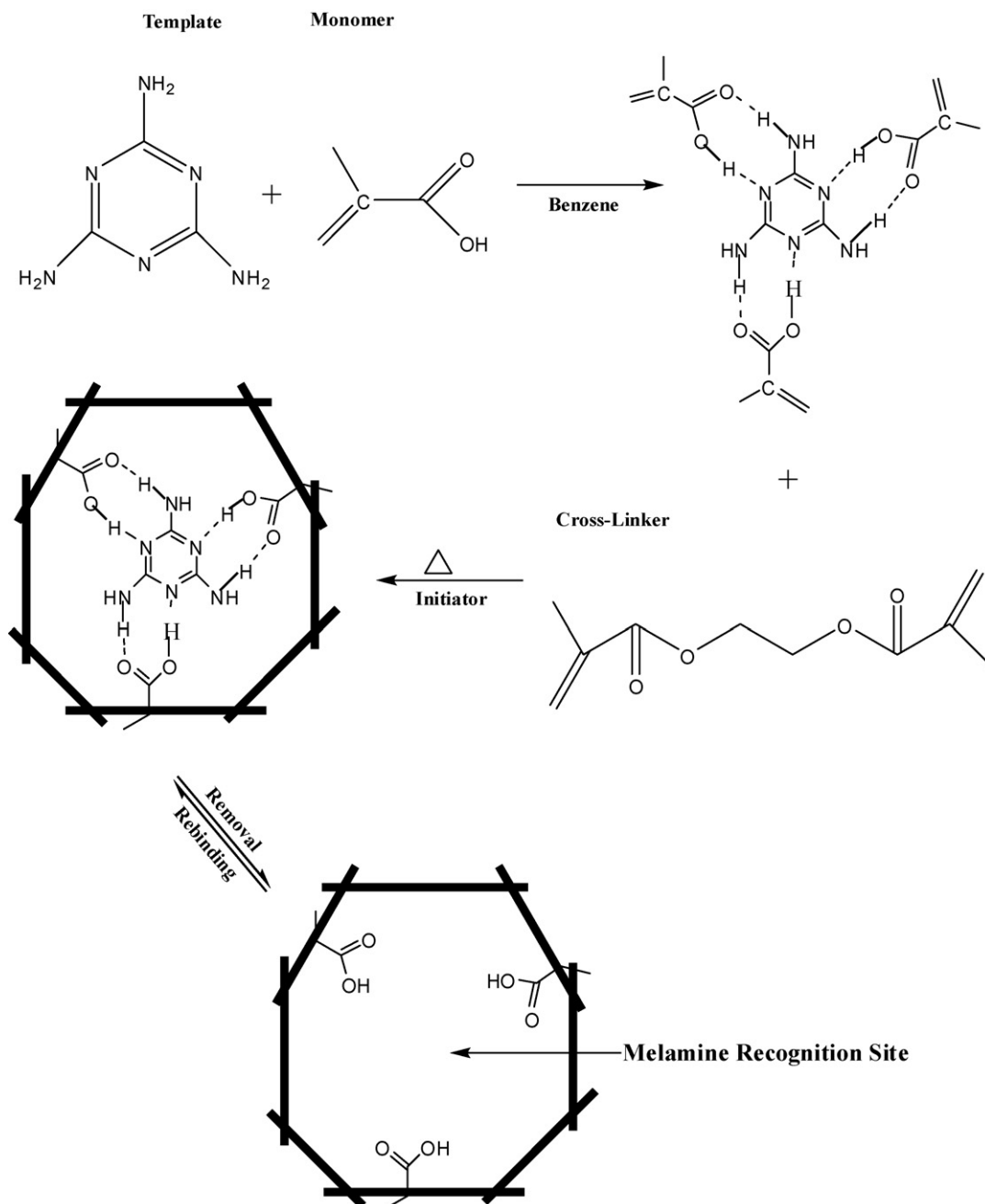

Fig. 1. Schematic representation of MIP synthesis.

de-ionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system. A stock solution of 0.01 M melamine was made by dissolving 1.261 g of melamine in 1 L of 0.05 M acetic acid solution. MAA, EGDMA, benzene and THF were distilled in vacuum prior to use. All other reagents were analytical grade and used without any further purification.

2.2. Synthesis of MIP

The schematic representation of the non-covalent imprinting process and removal of template is shown in Fig. 1. The MIP was prepared by the non-covalent method. Firstly, pre-complexation was obtained by mixing melamine (0.2 mmol) template and MAA (0.8 mmol) functional monomer with benzene (100 mL) in a 250 mL flask and sonicating for 10 min to maintain homogeneity. Secondly, EGDMA (2.4 mmol) and AIBN (1 mmol) were dropped into the flask as a cross-linker and an initiator, respectively, and then the resulting mixture was purged with N_2 for 5 min and sonicated for 10 min. Lastly, the flask was sealed under N_2 atmosphere and placed in an oil bath at 80 °C for 17 h for polymerization. The produced polymer was crushed, grounded and sieved to particle sizes ranging from 50 to 150 μm. Removal of the template and unreacted monomers was done by washing the polymer successively in methanol/acetic acid solution (8:2, v/v) for three times, each time for 3 h, and then twice in 70 °C de-ionized water for 2 h. The recycle time (~6 times) for washing process was finished until no absorption of the de-ionized water at 235 nm was observed with a Beckman DU-800 UV spectrophotometer. The non-imprinted polymer (NIP) was synthesized by the similar procedure in the absence of template molecules.

2.3. Preparation of membranes and ISEs

Membrane contained (in wt%) MIP or NIP (6.1), NaTFPB (1.5), NPOE (61.1), and PVC (31.3). The components of each membrane (totaling 360 mg) were dissolved in THF (3.5 mL) and poured into a glass ring (i.d. 36 mm) fixed on a glass plate. Overnight evaporation of the solvent yields membranes of ~200 μm. For each electrode, a disk of 9-mm diameter was punched from the membranes and glued to a plasticized PVC tubing with THF/PVC slurry. For measurement of melamine, the internal filling and conditioning medium were 10^{-4} mol L^{-1} melamine in 0.02 M acetate buffer of pH 3.7, while for measurement of experimental selectivity coefficients, 0.01 M NaCl was used as the internal filling and conditioning medium. All the electrodes were conditioned for one day before measurement.

2.4. Preparation of ion-exchanger column

1.5 g of 717-type anion-exchanger resin and that of 732-type cation-exchanger resin were treated with 25 mL of 1 M NaOH and 1 M HCl, respectively, equilibrating for 12 h under constant agitation. The resulting 717 hydroxide-form anion-exchanger resin and 732 hydrogen-form cation-exchanger resin were washed with de-ionized water and then packed separately in a 10-cm length of glass column (5.0 mm i.d.) and furnished with glass wool at both ends to retain the resins. The two columns were tandem connected for sample separation.

2.5. Sample pretreatment

Prior to sample analysis, 10 mL of ethanol was added into the same amount of milk sample. The mixture was centrifuged at 15,000 rpm and the supernatant was filtered through a standard 0.45 μm filter in order to remove the proteins which might interfere with the measurement probably due to its adsorption on the
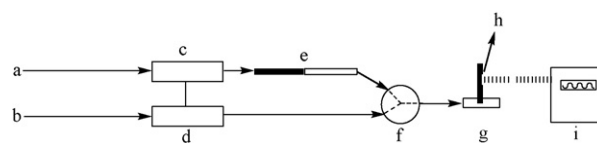

Fig. 2. Schematic diagram of the flow analysis system for the determination of melamine in pretreated milk samples: (a) sample solution; (b) buffer solution; (c) pump 1; (d) pump 2; (e) ion-exchanger tandem columns; (f) Y-joint; (g) flow cell; (h) ion-selective electrode; (i) recorder.

surface of membrane electrode, as reported by Ramamurthy et al. [28,29].

2.6. Potentiometric measurements

All measurements of emf were performed at 20–21 °C using a PXSJ-216L pH meter (Leici, Shanghai) with a saturated calomel electrode (SCE) as reference electrode in the galvanic cell: SCE//sample solution/ISE membrane/inner filling solution/3 M KCl/AgCl/Ag. Melamine standards were prepared by consecutively diluting 0.01 M of melamine with 0.02 M acetate buffer of pH 3.7. Selectivity coefficients were determined by the separate solution method in metal chloride solutions. The activity coefficient of ions, γ, was calculated from the modified Debye-Hükel equation:

$$\log \gamma = -0.511z^2 \left[\frac{\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} - 0.2\mu \right]$$

where μ is the ionic strength and z is the valence of the concerned ion.

2.7. General procedure

The apparatus manifold employed is shown in Fig. 2. The sample stream was delivered by one peristaltic pump (IFIS-D, Xi'an Remex Analyse Instrument Co., Ltd.) to flow through the ion-exchanger resin columns at a relatively low flow rate of 0.5 mL min^{-1} for efficient removal of interfering ions co-existing in milk. The de-ionized sample solution was merged at a Y-joint with 0.02 M acetate buffer solution of pH 3.7 delivered by another peristaltic pump at a flow rate of 1.0 mL min^{-1} to produce protonated melamine, which was then measured by the MIP based ISE placed in a flow cell (200 μl). PTFE tubing (0.8 mm i.d.) was used throughout the procedure to connect all components in the flow system.

3. Results and discussion

3.1. Effect of membrane ingredients

The influence of membrane composition on the potential response was tested and the results are shown in Table 1. Since the plasticizer/PVC ratio of about two results in suitable performance characteristics [30], this ratio was kept constant in the optimization of membrane composition. It was found that the membrane with NPOE provided a better response with a wider linear response range (5.0×10^{-6} to 1×10^{-2} M) compared to those with DOS (1.0×10^{-5} to 1×10^{-2} M) and DOP (1.0×10^{-4} to 1×10^{-2} M). Since lipophilic salts or ionic additives can decrease the membrane resistance, reduce anion interference and improve selectivity of the electrode [31], NaTFPB was incorporated in the membrane. Experiments show that the response slope of the MIP based membrane can be improved to be nearly theoretical with the lipophilic borate. The sensitivity and linearity for the membrane electrode also depends on the amount of MIP which determines the number of the binding sites. It can be seen that the potential sensitivity increases upon increasing the amount of MIP. However, at amounts above 6.1 wt%,

Table 1
Optimization of membrane composition of the melamine ISE.

PVC (wt%)	Plasticizer (wt%)			Borate (wt%)	MIP (wt%)	Linear range (mol L^{-1})	Slope[a] (mV decade^{-1})
	NPOE	DOS	DOP				
31.8	62.1	–	–	0	6.1	1.0×10^{-4} to 1.0×10^{-2}	9.2 ± 0.5
31.5	61.4	–	–	1	6.1	1.0×10^{-5} to 1.0×10^{-2}	50.2 ± 0.3
31.3	61.1	–	–	1.5	6.1	5.0×10^{-6} to 1.0×10^{-2}	54.1 ± 0.7
31.0	60.9	–	–	2.0	6.1	1.0×10^{-5} to 1.0×10^{-2}	49.1 ± 0.5
33.3	65.2	–	–	1.5	0	1.0×10^{-3} to 1.0×10^{-2}	49.5 ± 0.8
32.2	63.1	–	–	1.5	3.2	5.0×10^{-5} to 1.0×10^{-2}	49.8 ± 0.1
31.0	60.9	–	–	1.5	7.2	1.0×10^{-5} to 1.0×10^{-2}	50.7 ± 0.2
31.3	–	61.1	–	1.5	6.1	1.0×10^{-5} to 1.0×10^{-2}	39.0 ± 0.5
31.3	–	–	61.1	1.5	6.1	1.0×10^{-4} to 1.0×10^{-2}	40.3 ± 0.2

[a] Average from three electrodes ± standard deviation.

MIP becomes insoluble in the membrane which may cause low electrical conductivity and poor sensor response. Table 1 indicates that the membrane with 31.3 wt% of PVC, 61.1 wt% of NPOE, 1.5 wt% of borate and 6.1 wt% of MIP shows the best performance.

3.2. Effect of degree of cross-linking

Degree of cross-linking is the mole ratio of cross-linker/ monomer during polymerization process, which is essential for the formation of binding sites. The stable shape of complementary cavity for imprinted process cannot be maintained with low degree of cross-linking. However, high degree of cross-linking may result in difficulties in removal of template from the polymer and insolubility of MIP in the solvent [32]. To choose a suitable degree of cross-linking for polymerization process, the effect of the mole ratio of cross-linker/monomer was investigated in the range of 1–5. Fig. 3 shows that the variation of degree of cross-linking exhibits a significant difference in the potential response, and the mole ratio of 3 gives the best response in terms of wider linear range and lower detection limit.

3.3. Effect of pH

The influence of sample pH on the potential response of MIP based melamine ISE was tested with melamine of 10^{-4} and 10^{-3} M in the pH range of 1.5–7.0. The results are shown in Fig. 4. It can be seen that the potential response is nearly constant in the pH range of 3.0–4.5, but potential decreases appear at pHs beyond this range. This is probably due to the fact that at pH > 4.5, melamine mainly exists as a neutral molecule which shows no potential response at

ISE; but at pH < 3, melamine can be hydrolyzed and converted to other species such as ammeline and cyanuric acid [33], which leads to the decrease of the amount of protonated melamine ions.

3.4. Calibration curve

The potential response curves of MIP- and NIP-based membranes and the blank membrane (only with borate) are shown in Fig. 5. The MIP based membrane shows a near-Nernstian response of 54.1 mV/decade over the concentration range of 5.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a detection limit of 1.6×10^{-6} mol L^{-1}. However, the NIP-based and blank membranes exhibit a near-Nernstian response in a rather narrow concentration range, which is probably due to the nonspecific interaction of the protonated melamine ion with the ion-exchanger in the polymeric membrane. Evidently, it can be demonstrated that the MIP is effective for specific recognition of the target ion.

3.5. Response time and stability

The response time of the MIP based membrane ISE is defined as the average time required for the sensor to reach ±1 mV of the magnitude of the equilibrated potential signal after successively immersing in a series of melamine ion solutions, each having a 10-fold concentration difference [34]. The dynamic potential response with time is shown in Fig. 6, where the melamine concentration is changed between 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1}. It can be seen that the response of the MIP sensor is rapid (~16 s) and fully reversible. Experiments also showed that no significant changes
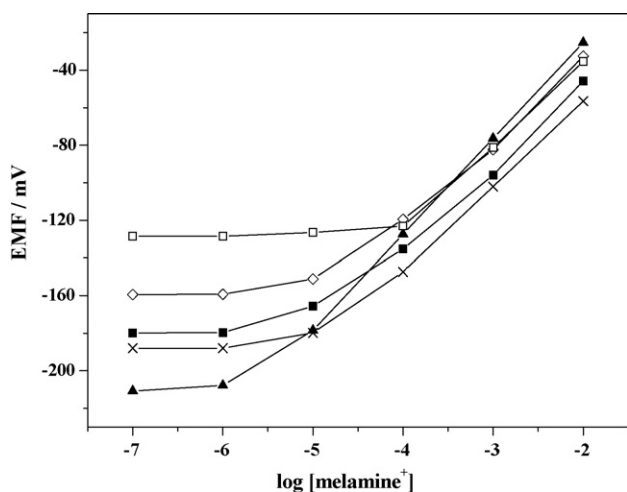

Fig. 3. Effect of degree of cross-linking on the potential response. The mole ratios of cross-linker/monomer are (■) 1, (◇) 2, (▲) 3, (×) 4 and (□) 5.
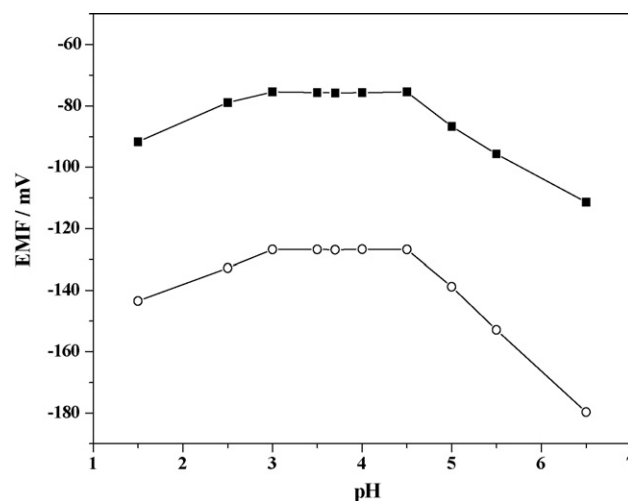

Fig. 4. Effect of pH on the potential response for melamine solutions: (■) 1.0×10^{-3} M and (○) 1.0×10^{-4} M.
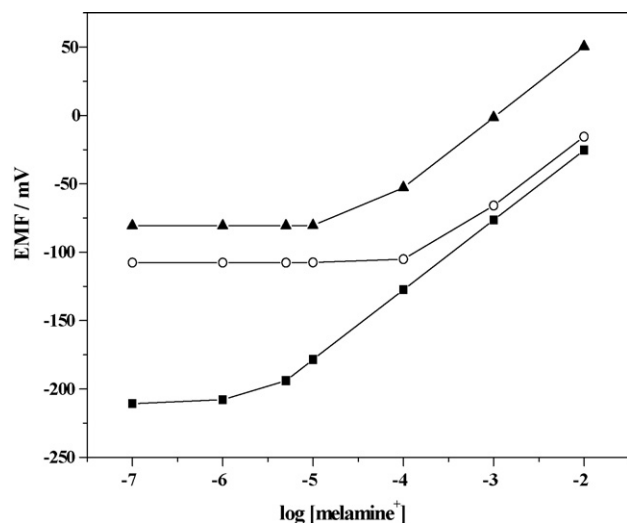
Fig. 5. Calibration curves for (■) MIP, (▲) NIP and (○) blank membranes. Membrane ingredients: MIP membrane, 31.3 wt% PVC, 61.1 wt% NPOE, 1.5 wt% NaTFPB and 6.1 wt% MIP; NIP membrane, 31.3 wt% PVC, 61.1 wt% NPOE, 1.5 wt% NaTFPB and 6.1 wt% NIP; blank membrane, 32.8 wt% PVC, 65.7 wt% NPOE and 1.5 wt% NaTFPB.

were observed in the response characteristics of the MIP-based melamine ISE after the electrode was stored in the conditioning solution for 2 months. Since ethanol is added to the sample solution for protein removal during the pretreatment procedure, the durability of the membrane electrode in ethanol solution was evaluated by measuring the response to the protonated melamine after storage in the ethanol/H_2O solution (1:4, v/v) for 24 h. No loss of response was observed for the proposed electrode after this time.

3.6. Selectivity coefficients

The selectivity coefficients ($K_{M,X}^{pot}$) for melamine (M) toward interfering ions (X) were evaluated by using the "strong interference" method introduced by Bakker to eliminate the influence of the inherent sensitivity limit on the ISE response toward discriminated ions [35]. The results of selectivity of MIP based ISE towards discriminated ions are shown in Fig. 7. Potentiometric selectivity coefficient values for the MIP or NIP-based ISE are summarized in Table 2. It can be seen that the proposed electrode shows high selectivity to melamine ion over other cations such as Na$^+$, K$^+$, H$^+$,
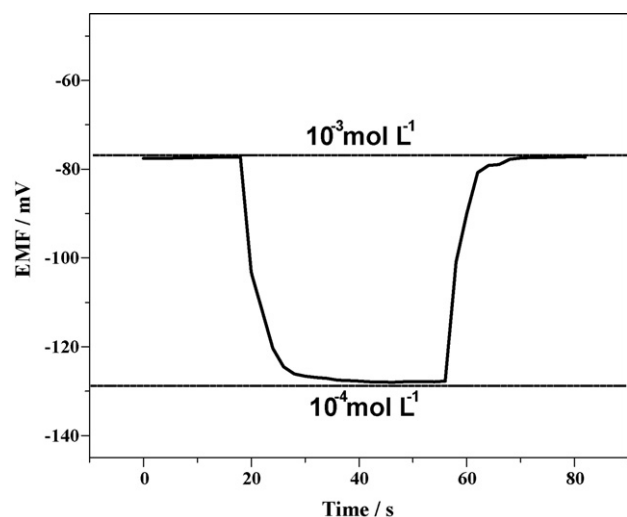

Fig. 6. Dynamic potential response of the MIP based ISE.

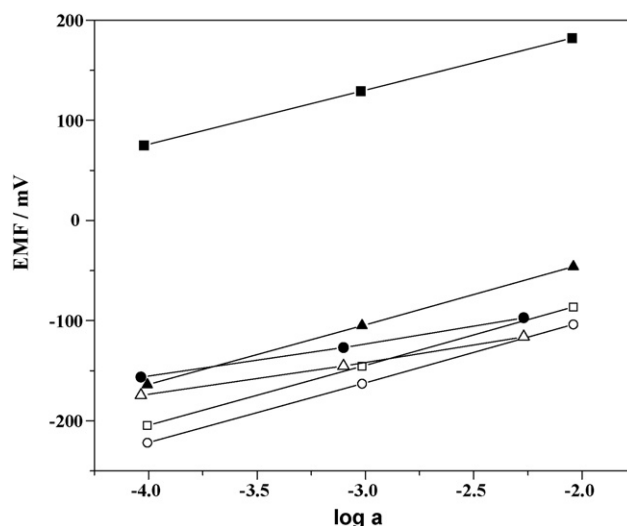**Fig. 7.** Potential responses of MIP based ISE according to Bakker's method toward cations: (■) protonated melamine (▲) K$^+$, (□) Na$^+$, (○) H$^+$, (●) Mg^{2+} and (△) Ca^{2+}.

Ca^{2+} and Mg^{2+}. The selectivity coefficients of the proposed MIP membrane electrode over interfering ions such as Na$^+$ and K$^+$ are superior to those of the NIP membrane electrode due to the specific recognition of the MIP for the target ion.

3.7. Interference study for pretreated milk samples

Milk samples contain rather high concentrations of interfering ions such as ∼10^{-2} mol L^{-1} of Na$^+$, K$^+$ and Ca^{2+}, therefore it is necessary to employ the ion-exchanger resin columns in the flow system to eliminate the interference of anion and cation co-existing in milk samples. Since melamine exists as neutral molecules [33] in milk samples with a pH of ∼6.7, it could flow through the ion-exchanger column without any loss. The effect of the ion-exchanger columns for measurement of melamine in pretreated milk samples is shown in Fig. 8. It can be seen that the flow system with the ion-exchanger columns indeed shows a wider linearity range of 1.5×10^{-5} to 1.0×10^{-2} mol L^{-1} and a lower detection limit of 6.0×10^{-6} mol L^{-1}, as compared to that without the columns which suffers from serious interference problems and has a rather poor detection limit of 1.2×10^{-4} mol L^{-1}. Experiments also indicate that the anion-exchanger column should be placed ahead of the cation-exchanger column for the tandem sequence. Such design can avoid the formation of acid solution (pH < 3) when the sample flows through the cation-exchanger column and exchange the co-existing cations with H$^+$ on the resins, which may cause the decomposition of melamine as discussed before. It should be noted that the response slope for measurement of protonated melamine in the pretreated milk samples (∼47.2 mV/decade) is a bit lower than that

Table 2
Potentiometric selectivity coefficients $K_{M,X}^{pot}$ for the MIP-based melamine ISE.

Interfering ion, X	log $K_{M,X}^{pot}$ [a]	Interfering ion, X	log $K_{M,X}^{pot}$
Na$^+$	−4.65 (−3.17)[b]	Ca^{2+}	−9.30
K$^+$	−3.96 (−3.04)[b]	Mg^{2+}	−8.67
H$^+$	−4.95	Cu^{2+}	−8.84
Li$^+$	−4.80	Fe^{2+}	−8.78
Tris$^+$	−3.97	Zn^{2+}	−8.92

[a] Mean values obtained from three corresponding pairs of concentrations of protonated melamine and the respective interfering cation in the Nernstian response range.

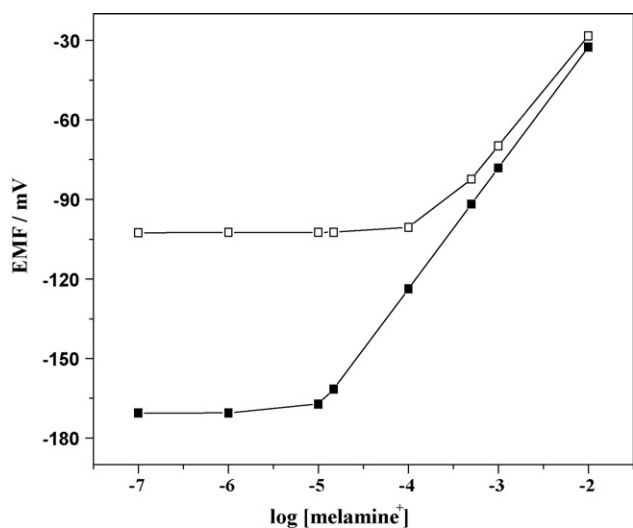[b] Values in the parentheses are the selectivity coefficients for the NIP membrane electrode.

Fig. 8. Potential responses of the flow system (■) with and (□) without the ion-exchanger columns for pretreated milk samples.

Table 3
Application of the proposed method to determination of melamine in milk samples spiked with different amounts of melamine.

Sample	Concentration of melamine ($\mu g\,mL^{-1}$)		Recovery (%)
	Amount added	Amount found[a]	
Milk 1	15.5	14.8 ± 0.5	95
Milk 2	8.9	9.6 ± 0.3	108
Milk 3	6.3	6.9 ± 0.1	110
Milk 4	3.2	3.0 ± 0.1	96

[a] Average value of three determinations ± standard deviation.

of the standard calibration curve (~54.1 mV/decade) for measurement in buffer solution, which is probably due to the matrix effect caused by the addition of ethanol to the sample solution during the pretreatment procedure.

The lifetime of the ion-exchanger column was calculated by the theoretical capacities of the cation-exchanger and anion-exchanger resins (4.2 and 3.0 mequiv. g^{-1}, respectively, as reported by the manufacturer). It can be estimated that the ion-exchanger column would be used for *ca.* 100 times.

3.8. Analysis of spiked milk samples

The flow analysis system based on the MIP based membrane electrode was used to analyze melamine in spiked milk samples which was pretreated with protein removal. The results are given in Table 3. It can be seen that the recoveries of on-line analysis of milk samples vary from 95% to 110%, indicating that the proposed MIP based sensor flow system has promising feasibility for rapid determination of melamine in complex samples even in the presence of relatively high concentrations of potential interferents.

4. Conclusions

A new polymeric membrane ion-selective electrode based on MIP for melamine has been described. Combined with flow analysis, the sensor can be used for measuring melamine in milk samples. The whole analysis including sample pretreatment takes less than 15 min and the detection limit is 6.0×10^{-6} mol L^{-1}, which satisfy the needs for on site rapid monitoring of trace melamine in milk. The flow analysis system is promising for use of detection of melamine contamination in other foods such as eggs and animal feeds.

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