

## A Silver Ion Potentiometric Sensor Based on a Synthesized 1,3-Benzocrown Macrocylic Diamide as Neutral Carrier

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**A synthesized benzo-crown macrocycle, 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione (1,3-MDA), was employed as an ionophore in the fabrication of polymeric ion-selective electrodes (ISE) for silver ion. The electrode membrane ingredients consisting of PVC/Plasticizer (*o*-NPOE) ratio of 0.94 and ionophore/additive ratio of 2.0 exhibited near Nernstian response of 57.75 mV/decade activity of Ag<sup>+</sup> over a linear concentration range of 10<sup>-6</sup> M to 10<sup>-3</sup> M (R<sup>2</sup> = 0.9921). The dynamic response time of this electrode was ~2 min at pH range of 3-9. The sensor has a limit of detection (LOD) of 6.32 x 10<sup>-7</sup> M, and was stable for at least one month. Initial investigation on the applicability of this new ISE for the detection of silver ions in photographic wastewater sample and comparison of its performance with conventional method (Atomic Absorption Spectroscopy) were also reported.**

Key Words: ionophore, macrocyclic diamide, potentiometry, PVC electrode, silver ion-selective electrode

### INTRODUCTION

Continuous interest has been focused on the design and synthesis of new functionalized macrocycles (Faridbod et al. 2007) for the selective detection of metal ions and its use as neutral carrier for ion-selective electrodes. After the discovery of valinomycin as ion carrier for K<sup>+</sup> ion, neutral organic compounds such as crown ethers (Ganjali et. al 2003), macrocyclic amides (Malinowska 2000) as well as macrocyclic calixarene compounds (Parsa et. al. 2007) have been used as ion carriers or ionophores for many polymeric membrane electrodes. Various macrocyclic diamides have been designed and tested for their utility as neutral ionophores in the construction of PVC-based ion-selective electrodes for various heavy (Shamshipur

2002; Singh and Bhatnagar 2003), Group IA (Shamshipur et. al. 2001) and Group IIA (Gupta et. al. 2003) metal ions. The selectivity of these various macrocyclic diamide ligands relies largely on the availability of the heteroatoms nitrogen, oxygen and sulphur, and their geometric complementarity with the target analyte.

The synthesis of sensing materials and its incorporation in the fabrication of ion selective electrodes (ISEs) is a simple yet inexpensive way of providing means to detect metal ions in solutions. Metal ion sensor technology combines the principles of hard-soft-acid-base (HSAB) chemistry (Pearson 1963) and potentiometry, and has always proved to be successful in metal ion analysis since its inception. The main advantage of ISEs over the conventional methods, such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma

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Mass Spectrometry (ICP-MS), is its simplicity and economy, as well as its ability to directly detect not the total ion concentration but the activity of the metal ion, which is important in both biological and environmental perspectives. Moreover, with the improvement of detection limits (Szigeti et al. 2006), ISE does not only show great promise as an ideal but also as an important technique which cannot be underestimated.

The use of silver and its compounds in electronic, electrical and photographic industries is well known. Some have also been used as antibiotics (Lansdown 2002), medical and cosmetic ingredients (Green and Su 1987). In terms of their health impact, trace amounts of this metal were found to deposit in some parts of the body such as skin, eye, liver, kidney, and oral tissues of experimental animals (Furchner et al. 1968). It has been implicated in some rare diseases (East et al. 1980) and its toxic effects at high amount have also been reported (Wagner 1975). Hence, the development of fast and sensitive methods for its detection and analysis cannot be understated.

In this study, thus, we synthesized and developed a new ionophore for silver ion based on a benzo-crown macrocyclic diamide. This paper describes the synthesis and characterization of 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione (1,3-MDA) and its subsequent incorporation as neutral carrier in polyvinyl chloride (PVC) membrane electrodes. The evaluation of the new ISE and its ability to detect silver ion in wastewater from photographic films were also described.

## EXPERIMENTAL SECTION

### Materials

Chemicals and reagents used for synthesis were purchased from Sigma-Aldrich and used as received. Reagent grade dioctyl phthalate (DOP), *o*-nitrophenyl octyl ether (NPOE), potassium tetrakis(4-chlorophenyl) borate (KTCIPB), tetrahydrofuran (THF) and high relative molecular weight PVC (Sigma-Aldrich, St. Louis, MO, USA) were used for the preparation of the membrane. The metal salts used for the selectivity studies were of the highest purity (Sigma-Aldrich, St. Louis, Missouri, USA; Merck, Darmstadt, Germany; J.T. Baker, Phillipsburg, NJ, USA). Solvents used for the synthesis and purification processes were used as received or redistilled as deemed necessary.

The target compounds, both intermediate and the desired products were synthesized using the modified sequential “two-pot” procedure (Hruby and Barstow 1971). Purification of the intermediate and product compounds were done using normal phase column chromatography

with silica gel ( $\Sigma$ 230-400 mesh, 40-63 $\mu$ ) as stationary phase and was monitored by thin layer chromatography (TLC). Likewise, solvent casting method was utilized in the preparation of the PVC-membrane electrode. All emf measurements were carried in magnetically stirred solutions at room temperature.

### Characterization

The melting point of the both intermediate and product were determined by the Differential Scanning Calorimetry (DSC). The molecular mass was measured in the negative mode using Finnigan MAT LCQ Mass Spectrometer (ESI-MS). The Fourier Transform-Infrared (FT-IR) spectra of the compounds (intermediate and the desired product) were obtained using IR Prestige-21 with KBr as reference.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR were recorded on JEOL LA FT NMR at 400 MHz using  $\text{CDCl}_3$  as solvent with trimethylsilane (TMS) as reference compound.

### Synthesis of 1,3-bis(*o*-amido-phenylhydroxy)propane

A mixture of triphenylphosphine (2.754 g, 10.5 mmol), and bromotrichloromethane (2.480 g, 12.5 mmol) in 30 mL THF was refluxed for 30 minutes at 60 °C. The mixture was allowed to cool to 5 °C, and salicylic acid (1.38 g, 10 mmol) dissolved in 10 mL THF was added. The solution was allowed to stand for 10 min, then, 1,3-diaminopropane was added rapidly (~5 s). The mixture was then heated gradually to 60 °C under reflux for 4–5 hr with continuous stirring. After cooling to room temperature, the mixture was removed from the reflux set-up and filtered. The supernatant was concentrated in a rotavap at 40 °C and the residue was redissolved in 150 mL dichloromethane (DCM) and washed with 1 M HCl (50 mL). After removing the aqueous portion, the organic part was again re-concentrated in rotavap (40 °C), and the residue was redissolved in diethyl ether (50 mL). The solution was transferred to a separatory funnel and 0.25 M NaOH (50 mL) was added. The aqueous solution was re-extracted with diethyl ether three times (50 mL), while discarding the organic layer. The aqueous layer was acidified with 6 M HCl to pH 2, and was again extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 mL). The  $\text{CH}_2\text{Cl}_2$  extracts were pooled and dried with anhydrous  $\text{MgSO}_4$ . After drying, the pooled extract was passed through a column (10 mm i.d. x 155 mm length) of 10-12 g silica gel (Silica Gel 60, Merck, 0.0063-0.200 mm), and was eluted with ethyl acetate/ $\text{CH}_2\text{Cl}_2$  (1:1). Fifty-milliliter portions of the eluent were obtained, and a few drops were spotted on TLC plates with ethyl acetate. The intermediate was found to be a yellowish oily liquid (**I**). The structure of this intermediate (shown in Figure 1) was confirmed by spectroscopy. The intermediate was used in the next step without further purification.

$C_{17}H_{18}O_4N_2$  (**I**): Yield, 8.3224 g (95%); TLC (1:1 ethyl acetate/ $CH_2Cl_2$ ),  $R_f$ (0.86). Spectroscopic data: MS (ESI-MS) –  $m/z$  at 314.2 [ $M$ ]<sup>+</sup>, 100%; IR (KBr)  $\nu_{max}$  – 3381  $cm^{-1}$  (N-H stretching secondary amide), 2400-3200  $cm^{-1}$  (O-H stretching) and 1634  $cm^{-1}$  (carbonyl C=O); <sup>1</sup>H- and <sup>13</sup>C-NMR – [<sup>1</sup>H-NMR (CH<sub>2</sub>-CH<sub>2</sub>-NH)  $\delta$  3.68 (t); (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  1.77(qt); (CH<sub>2</sub>-NH-CO)  $\delta$  8.92 (br, s); (CH(Ar) ortho to =C-C=O)  $\delta$  7.81 (d); (CH(Ar) meta to =C-C=O)  $\delta$  6.92 (t); (CH(Ar) meta to =C-O-)  $\delta$  7.12 (t); (CH(Ar) ortho to =C-O-)  $\delta$  6.62 (d); <sup>13</sup>C-NMR, (NH-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  36.55; (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  26.68; (NH-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  36.55; (NH-C=O)  $\delta$  169.79; (Ar)C=  $\delta$  114.74; ((Ar)C= ortho to =C-C=O)  $\delta$  127.0; ((Ar)C= meta to =C-C=O)  $\delta$  117.65; ((Ar)C= meta to =C-O-)  $\delta$  133.38; ((Ar)C= ortho to =C-O-)  $\delta$  116.0; (O-(Ar)-C=)  $\delta$  159.26; (NH-C=O)  $\delta$  170.0; ((Ar)C=)  $\delta$  114.7].

#### Synthesis of 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione (1,3-MDA)

The desired product, 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione or 1,3-MDA, was synthesized according to the modified Hruby and Barstow method (1971) as follows: Intermediate (**I**) obtained (5 mmol) from the previous method was mixed with Cs<sub>2</sub>CO<sub>3</sub> (10 mmol) in 20 mL dimethylformamide (DMF) and the mixture was stirred and heated to 120°C under reflux. A solution of 2-chloroether (7.5 mmol) in DMF was added dropwise to the mixture. The reaction was continued for 10-12 hr at 120°C with continuous stirring. After cooling, the solvent was distilled out over vacuum. Deionized water was then added to the residue, obtaining a white precipitate. The solid was washed again with deionized water and filtered, redissolved in DCM (100 mL) and dried over MgSO<sub>4</sub>. Purification was done by successive column (10 mm i.d. x 155 mm length) chromatography (over Silica Gel) using 150 mL CH<sub>2</sub>Cl<sub>2</sub> as eluant followed by ethyl acetate (EtOAc) Fractions were concentrated on rotavap (40°C) to obtain the product **II** (white powdery solid). By Differential Scanning Calorimetry (DSC) the product was obtained with a single sharp peak at a melting point of 194.1°C, indicating that it was of high purity.

$C_{21}H_{24}O_3N_2$  (**II**): Yield, 0.9376 g (74.14%); TLC (EtOAc),  $R_f$  = 0.85. Spectroscopic data: MS (ESI-MS) –  $m/z$  383.3 [ $M$ ]<sup>+</sup>, 100%; IR(KBr)  $\nu_{max}$  3323  $cm^{-1}$  (NH stretching, secondary amide), 1549  $cm^{-1}$  (N-H bending, C-N stretching amide functional group), 1639  $cm^{-1}$  (C=O stretching, amide carbonyl), <sup>1</sup>H- and <sup>13</sup>C-NMR analysis [<sup>1</sup>H-NMR: (CH<sub>2</sub>-NH-CO)  $\delta$  8.36 (br); (O-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  4.32 (t,  $J$  4.16); (CH<sub>2</sub>-CH<sub>2</sub>-O)  $\delta$  3.99 (t,  $J$  4.12); (CH<sub>2</sub>-CH<sub>2</sub>-NH)  $\delta$  3.55 (q,  $J$  5.84); (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)  $\delta$  2.03 (qt,  $J$  6.01); (CH(Ar) ortho to =C-C=O)  $\delta$  8.21 (dd,  $J$  1.48); (CH(Ar) meta to =C-C=O)  $\delta$  6.97 (d,  $J$  8.28); (CH(Ar) meta to =C-O-)  $\delta$  7.44 (t,  $J$  7.08, 6.84); (CH(Ar) ortho to

=C-O-)  $\delta$  7.12 (t,  $J$  7.56); (CH(Ar) ortho to =C-C=O)  $\delta$  8.21 (dd,  $J$  1.48); (CH(Ar) meta to =C-C=O)  $\delta$  6.97 (d,  $J$  8.28); (CH(Ar) meta to =C-O-)  $\delta$  7.44 (t,  $J$  7.08, 6.84); (CH(Ar) ortho to =C-O-)  $\delta$  7.12 (t,  $J$  7.56); (CH(Ar) ortho to =C-C=O)  $\delta$  8.21 (dd,  $J$  1.48); (CH(Ar) meta to =C-C=O)  $\delta$  6.97 (d,  $J$  8.28); (CH(Ar) meta to =C-O-)  $\delta$  7.43 (t,  $J$  7.08, 6.84); (CH(Ar) ortho to =C-O-)  $\delta$  7.12 (t,  $J$  7.56); <sup>13</sup>C-NMR: (NH-C=O)  $\delta$  165.22; ((Ar)C=)  $\delta$  122.12; (O-(Ar)C=)  $\delta$  156.35; (O-CH<sub>2</sub>-CH<sub>2</sub>-)  $\delta$  68.09; (CH<sub>2</sub>-CH<sub>2</sub>-O)  $\delta$  69.92; (CH<sub>2</sub>-CH<sub>2</sub>-O)  $\delta$  69.92; (O-CH<sub>2</sub>-CH<sub>2</sub>-)  $\delta$  68.09; (O-(Ar)C=)  $\delta$  156.35; ((Ar)C=)  $\delta$  122.12; (NH-C=O)  $\delta$  165.22; (NH-CH<sub>2</sub>-CH<sub>2</sub>-)  $\delta$  36.11; (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-)  $\delta$  27.81; (NH-CH<sub>2</sub>-CH<sub>2</sub>-)  $\delta$  36.11; ((Ar)C= ortho to =C-C=O)  $\delta$  132.30; ((Ar)C= meta to =C-C=O)  $\delta$  122.60; ((Ar)C= meta to =C-O-)  $\delta$  132.53; ((Ar)C= ortho to =C-O-)  $\delta$  113.04; ((Ar)C= ortho to =C-C=O)  $\delta$  132.30; ((Ar)C= meta to =C-C=O)  $\delta$  122.60; ((Ar)C= meta to =C-O-)  $\delta$  132.53; ((Ar)C= ortho to =C-O-)  $\delta$  113.04]

#### Preparation and Evaluation of Membrane ISE

The membranes were prepared by mixing 47 mg PVC, 50 mg NPOE, 2 mg ionophore and 1 mg KTpCIPB in 1 mL THF. The resulting mixture was thoroughly mixed in a vortex mixer and degassed in an ultrasonic bath for 10 min. The membrane mixture was poured in a glass ring (30 mm i.d. x 25 mm) resting on a glass plate. A pad of filter paper and glass slide were placed on top of the ring to facilitate controlled evaporation of the solvent. After two days, the membrane was gently peeled off the glass plate using a pair of forceps. Using a cork borer (10 mm i.d.), a portion of the membrane was cut-off and pasted on an acrylic tube with a PVC paste. After drying overnight, the PVC tube was filled with internal filling solution (1.0 x 10<sup>-3</sup> M AgNO<sub>3</sub>) and an anodized silver wire was inserted into the tube. Finally, the electrode was conditioned with 1.0 x 10<sup>-3</sup> M AgNO<sub>3</sub> for 4 days.

All emf measurements were carried in magnetically stirred solutions at room temperature (28-29 °C) using a Fisher pH/mV meter. An Orion (Cambridge, MA, USA) sleeve-type (Model 900200) double-junction Ag/AgCl was used as an external reference electrode. Electrode performance was examined by measuring the potentials of the solutions of the primary ion at concentration ranges of 10<sup>-6</sup> to 10<sup>-1</sup> M. Values of the selectivity coefficients ( $K^{pot}$ ) were obtained by Separate Solution Method (SSM, equation 1) (Umezawa et. al. 1995)

$$K_{ij} = \frac{a_i}{(a_j)^{z_i/z_j}} \exp\left\{\frac{E_j - E_i}{RT} z_i F\right\} \quad (1)$$

where

- $a_i$  - sample activity of the primary ion
- $a_j$  - activity of the interfering ion
- $Z_i$  - charge of the primary ion
- $Z_j$  - charge of the interfering ion
- $E_j$  - standard potential of the interfering ion
- $E_i$  - standard potential of the primary ion
- $R$  - Gas constant, 8.314 J/Kmol
- $T$  - Absolute temperature, K
- $F$  - Faraday constant, 96487 C/mole

and Match Potential Method (MPM, equation 2) (Gadzekpo and Christian 1984).

$$K_{IJ}^{MPM} = \frac{\Delta a_I}{a_J} \text{ where } \Delta a_i = a'_i - a_i \quad (2)$$

where

- $a_i$  - initial background activity of ion I
- $a'_i$  - activity of the reference solution (known concentration of the primary ion)
- $a_j$  - activity of the interfering ion

The electrodes were pre-conditioned with a 0.001 M solution of the primary ion for 1-2 days before use. Activities of the metal salt solutions were calculated using the Debye-Hückel equation (Craggs et. al. 1974). Detection limit of the electrode was obtained from the calibration curves according to IUPAC recommendations for ISEs (Buck and Lindner 1984).

## RESULTS AND DISCUSSION

### Synthesis of 1,3-MDA Ionophore

In this study, the ionophore (**II**), 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione (1,3-MDA), was synthesized such that its cavity diameter and its structure were flexible and rigid enough to accommodate heavy metal ions by adopting Hruby and Barstow (1971) method with some modifications (Figure 1). Spectroscopic characterizations revealed that 1,3-MDA was obtained in relatively high purity.

### Evaluation of Potentiometric Properties of 1,3-MDA

The ability of the synthesized ionophore to bind with several metal ions was investigated by preliminary selectivity screening of the 1,3-MDA PVC-based ISE. Initial computer simulation studies on the interaction of several metal with 1,3-MDA molecule showed that the ionophore was selective towards  $\text{Ag}^+$  ion (data not shown). On this basis, initial selectivity studies were done by fabricating the 1,3-MDA PVC-based membrane

electrode with the initial membrane formulation of 32 mg PVC, 65 mg *o*-NPOE as plasticizer, 2 mg ionophore (1,3-MDA) and 1 mg oleic acid (OA) as additive. The ISE showed to be sensitive towards monovalent cations, such as those belonging to the alkali group ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and  $\text{Ag}^+$  using  $10^{-4}$  M  $\text{Zn}(\text{NO}_3)_2$  ( $10^{-4}$  M  $\text{Zn}^{2+}$  as the primary ion) as internal filling solution (Figure 2). The ISE gave the most sensitive potential response with  $\text{Ag}^+$ , as indicated by the calculated  $K_{ij}$  values ( $\text{Zn}^{2+}$  as primary ion) (Figure 2). Table 1 shows the summary for the optimization of the membrane components.

### Effect of Plasticizer

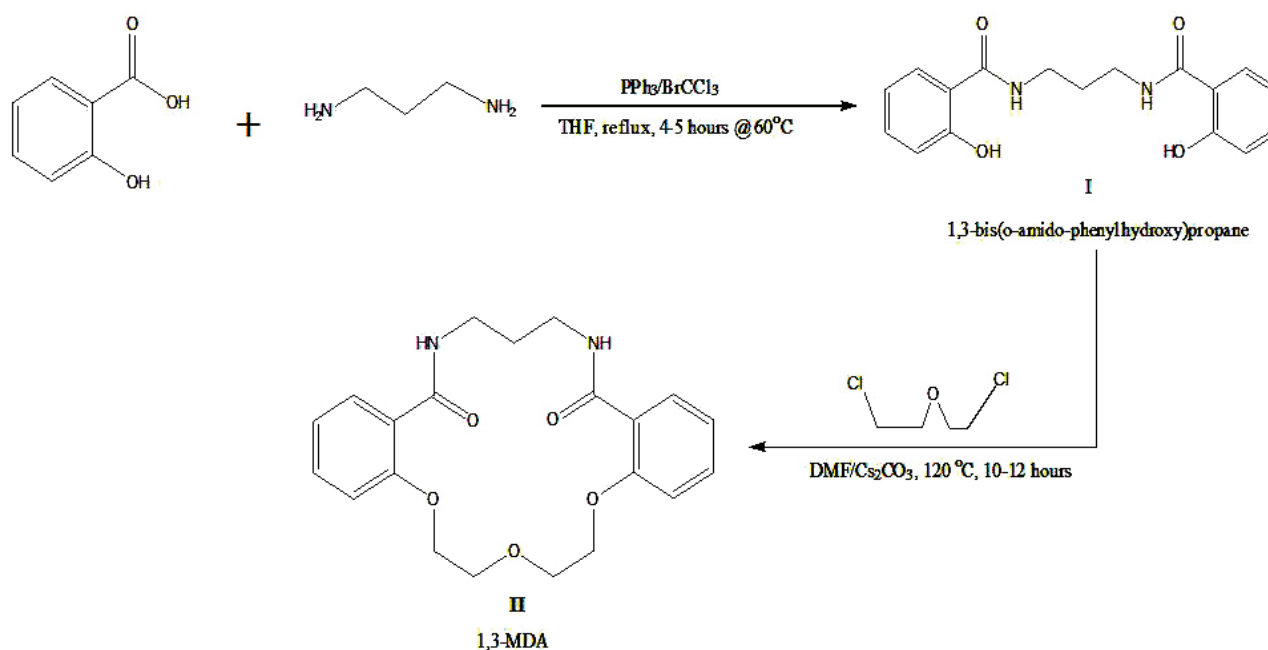
The most important factor in the extraction behaviour (selectivity and sensitivity) of ISEs involved the membrane composition, which in turn depends upon the proper PVC-to-plasticizer ratio. To obtain the optimum PVC-to-plasticizer ratio, different types of plasticizers were used (*o*-NPOE, DOP, DBP and DBS) and their ratios were changed from 0.49 to 1.3, while keeping the ionophore-to-additive ratio constant. As shown in Figure 3A, each of these plasticizers influenced differently the membrane ISE's response to  $\text{Ag}^+$ , which might be due to their differences in polarities: *o*-NPOE ( $\epsilon = 24$ ), DOP ( $\epsilon = 7$ ), DBP ( $\epsilon = 6.4$ ) and DBS ( $\epsilon = 4.5$ ). Of all the membrane electrodes, the one with *o*-NPOE responded Nernstianly (steepest) with a slope of 57.745 mV/decade activity of  $\text{Ag}^+$  over a wider linear concentration range (Figure 3A). The most sensitive, reproducible and stable response was obtained at a PVC-to-plasticizer ratio of 0.94. The result implies that very high amount of PVC or polymer membrane could not provide a suitable environment for  $\text{Ag}^+$  ion selectivity. Apparently, judging from the ratio, a near equivalent amount would contribute to its selectivity.

The nature of plasticizer (solvent mediator), the plasticizer-to-PVC ratio, nature and amount of ionophore and additives used would greatly influence the sensitivity and selectivity of the membrane electrode (Mahajan and Sood, 2007). The relatively better sensitivity of the fabricated  $\text{Ag}^+$ -ISE was due to the high dielectricity imparted by *o*-NPOE to the membrane phase (Shamsipur et. al. 2002), which may lead to considerable mobility of the  $\text{Ag}^+$  ions within the membrane (Mahajan and Sood, 2007). Also, *o*-NPOE provides suitable elasticity to the membrane compared to the other plasticizers with less permittivity for facile exchange of ions within the membrane.

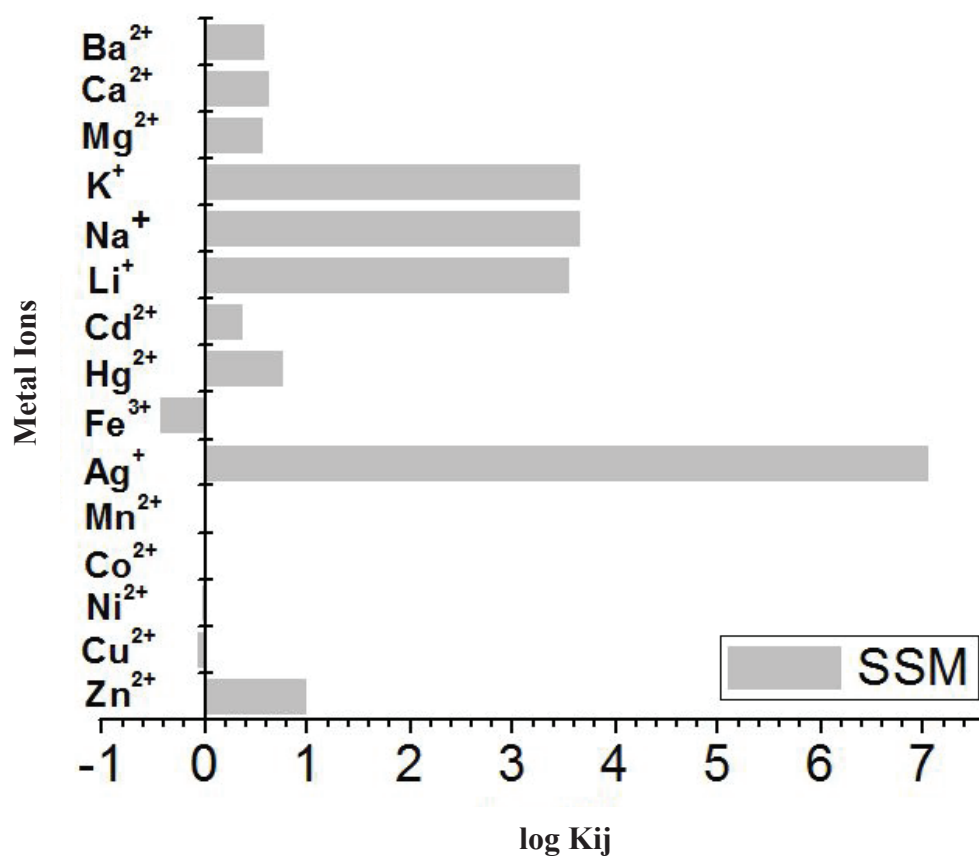
### Effect of Lipophilic Additives

The effect of incorporating other membrane components such as anion suppressor (potassium tetrakis(4-chlorophenyl) borate, KTCIPB), OA (oleic Acid) and





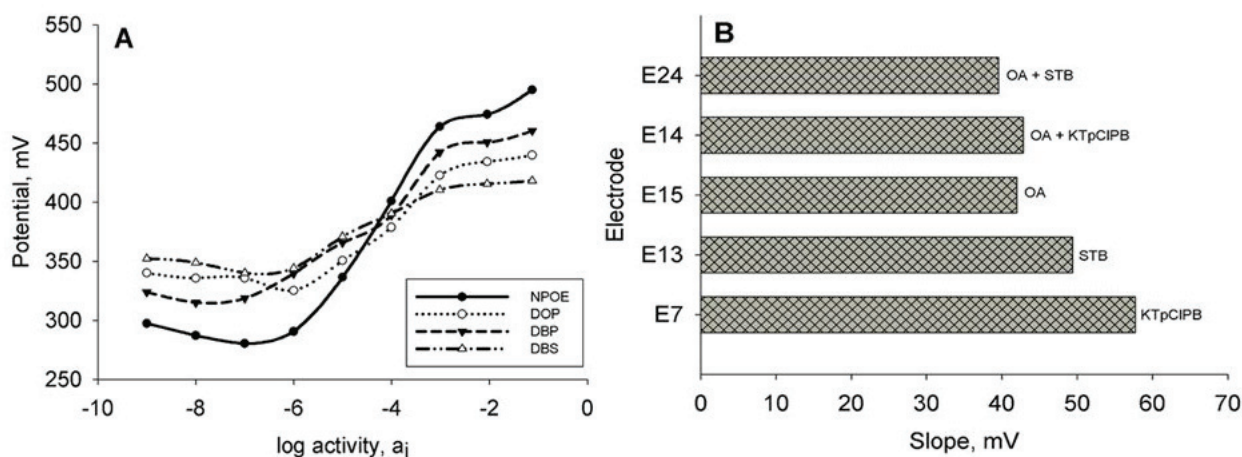
**Figure 1.** Sequential two-pot procedure for the synthesis of 1,15-diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione (1,3-MDA)



**Figure 2.** Screening of ion selectivity of the 1,3-MDA-based ISE using 10<sup>-3</sup> M Zn<sup>2+</sup> as the internal filling solution (SSM-Separate Solution Method)

**Table 1.** Optimization of membrane components

Electrode No.	% Composition				Linear Range (M)	Slope
	PVC	Plasticizers	1,3-MDA	Anion Suppressors		
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	56.295
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.63
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.413
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.745
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.138
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.141
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	56.679
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	56.083
7	47	50, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	55.23
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.519
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	57.27
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	55.709
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	55.997
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	55.377
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	55.599
8	51	46, NPOE	2	1, KTCIPB	$10^{-6}$ - $10^{-3}$	54.954



**Figure 3.** Influence of membrane components on the potentiometric response of the  $\text{Ag}^+$ -ISE. (A) Effect of plasticizers on the potentiometric response of the  $\text{Ag}^+$ -ISE (DBP- dibutyl phthalate; DBS- dibutyl sebacate; DOP- dioctyl phthalate, NPOE-o-nitrophenyl octyl ether); (B) Effect of anion suppressors (KTPCIPB – Potassium tetrakis(4-chlorophenyl) borate; STB – Sodium tetraphenyl borate; OA – Oleic Acid)

sodium tetraphenylborate (STB) was investigated to see if the potentiometric response and sensitivity of the electrode would be affected. Our experiments indicated that the addition of KTCIPB improved the sensitivity of the electrodes (Figure 3B). The incorporation of 1% KTCIPB as a lipophilic anion suppressor greatly improved the response behavior of the electrode. Thus, the electrode with a membrane composition of 47:50:2:1 % (PVC:*o*-NPOE:Ionophore:KTCIPB) was chosen to be

the optimum formulation and was used throughout this study (Table 1).

In cases where the extraction behavior of an ionophore is poor, the presence of additives could greatly enhance the sensitivity of an ISE (Shamsipur et al. 2002). Generally, lipophilic additives were introduced in order to reduce interference of lipid-soluble sample anions (Mahajan and Sood 2007). These additives would lower the electric

membrane resistance as well as the activation barrier for the cation-exchange reaction at the membrane-solution interface (Shamsipur et al. 2007). This would also help in the cation-exchange kinetics within the sample-membrane interface (Shamshipur et. al. 2007).

### Selectivity

To validate the selectivity of the new electrode towards silver ion, matched potential method (MPM) (Figure 4) was compared to Separate Solution Method (SSM) with  $10^{-3} M Ag^+$  as internal filling solution (refer to Equation 1 and Equation 2 for SSM and MPM, respectively). The results suggested that the proposed ISE was very selective towards  $Ag^+$  by both methods. Though the trend in MPM suggested that higher oxidation transition state (TS) metal ions ( $Sn^{4+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Ce^{3+}$ ,  $Cr^{3+}$ ) were likely to interfere in the activity of  $Ag^+$  ion in mixed solution, their negative  $K_{ij}$  values implied that these could barely occur at the experimental conditions given. MPM was considered as closer to the 'real solution' state than SSM, since interference ion could be introduced to the solution containing the analyte ion to evaluate

quantitatively the ISE's selectivity towards the latter (Gadzekpo and Christian 1984). Moreover, the trend in MPM was in good agreement with the HSAB theory by Pearson (1963). Hard acids (and hard bases) are those that have small size and higher oxidation states such as those ions mentioned, and in a competitive situation, hard acids tend to form complexes with hard base ligands. In addition, higher oxidation state metal ions are known to have stronger or greater ability to attract electrons towards them (Pearson 1963). Thus, in real system, these ions would interfere in the complexation of the analyte ion with the ligand due to the formation of strong intermolecular forces with the donor atoms in the ring, such as oxygen or nitrogen.

Though the trend in SSM was not similar to that of MPM, the calculated  $K_{ij}$  values for both methods were in good agreement that the proposed membrane electrode was selective towards  $Ag^+$  over other metal ions tested, corroborating with our preliminary selectivity screening. Hence, we proceeded to evaluate the  $Ag^+$ -ISE's performance characteristics.

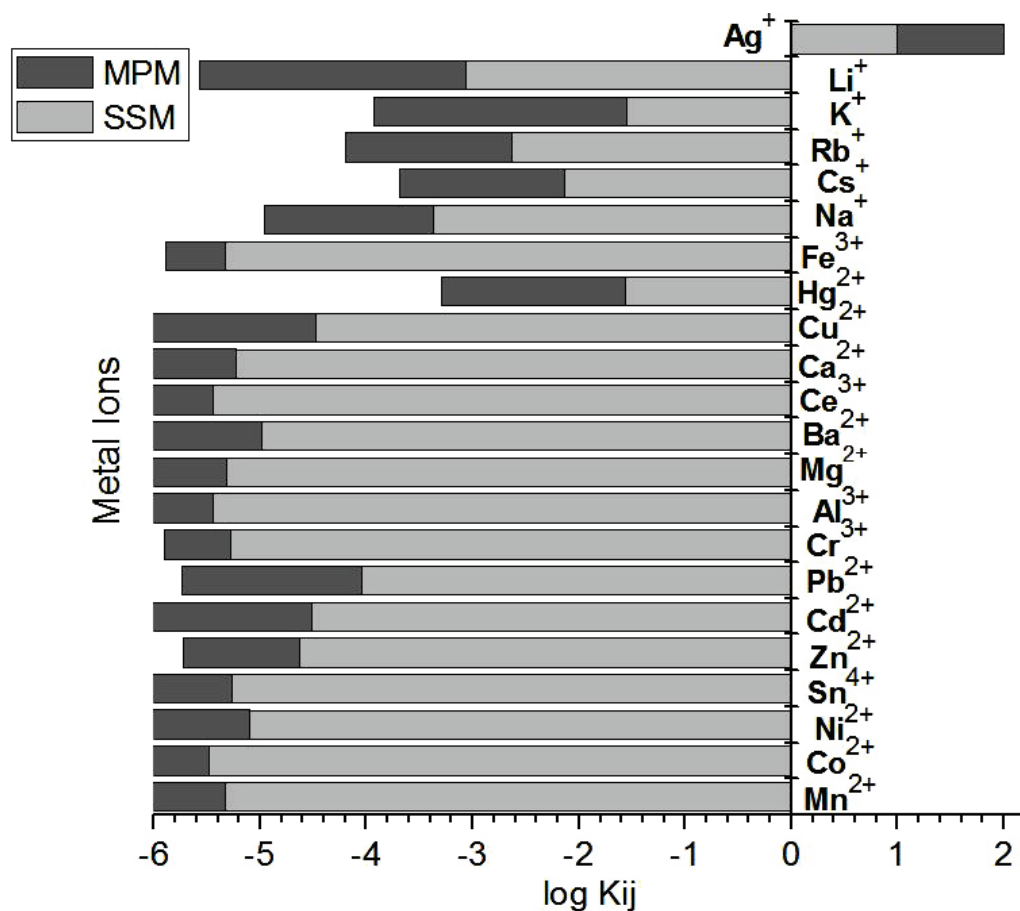


Figure 4. Selectivity coefficients of the new  $Ag^+$ -ISE based on 1,3-MDA using  $10^{-3} M Ag^+$  internal filling solution. (SSM-Separate Solution Method; MPM-Matched Potential Method)

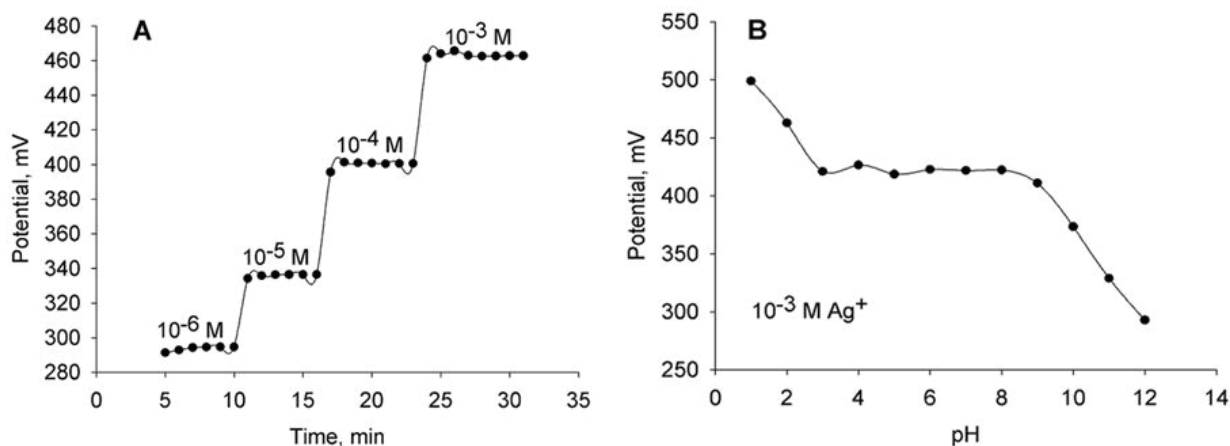
### Electrode Response Characteristics

The potentiometric response characteristics of electrodes with different compositions were evaluated and summarized in Table 1. The most sensitive electrode response was obtained with E7 (membrane composition: 0.94 PVC-to-plasticizer ratio; 2.0 lipophilic additives ratio; 2 mg amount of ionophore) at 57.75 mV/decade activity ( $R^2 = 0.9921$ ) and linear range from  $10^{-6}$  to  $10^{-3}$  M. Using a very stringent requirement of  $\pm 0.1$  mV to reach the final equilibrium, the optimum conditioning period for Electrode No. E7 was four days, after which the ISE generated stable potential response ( $\sim 2$  min) when placed in contact with  $Ag^+$  solutions ( $1.0 \times 10^{-3}$  M  $AgNO_3$ ). As shown in Figure 5A, the average response time (2 min) of the proposed ISE (criterion:  $\pm 0.1$  mV of the final equilibrium value after successive immersions of a series of  $Ag^+$  ions) indicates the sensitive time dependence of the electrode response towards minute changes in the electrolyte composition.

Likewise, the pH dependence of the fabricated electrode was shown in Figure 5B. The electrode response was independent of pH within the range of 3-9, beyond which the potential decreases dramatically (pH 1-2 and 10-12). At pH 1-2, the hydronium ions ( $H_3O^+$ ) might

compete with the  $Ag^+$  on the electrode surface, while at pH 10-12 hydroxide ions might complex with  $Ag^+$  ions in the solution, thus, suppressing electrode response. Furthermore, the working or linear range of the proposed  $Ag^+$ -ISE was established between  $10^{-6}$  –  $10^{-3}$  M  $AgNO_3$  with a near Nernstian slope (average of four calibrations) of 57.43 mV/decade activity of  $Ag^+$  (Figure 6A). This near Nernstian value (57.43 mV) was close to the theoretical value (59 mV) for monovalent cation, which may indicate an efficient ligand-metal complexation. At the working concentration range, the calibration line gave a very good linearity of  $R^2 = 0.9921$  indicating a good correlation between the activity of the  $Ag^+$  ion and the emf response.

The average detection limit for Electrode No. E7 was  $6.76 \times 10^{-7}$  M, which was determined from the intersection of the two extrapolated straight line of the calibration graph (Figure 6A) and relatively comparable to other fabricated ISE's based on macrocyclic diamides as ionophore (Table 2). This might be due to the smaller complex formation of the chosen ionophore to the metal ions, which reduces the tendency of an increase of primary ion concentration in the sample (Lindner and Umezawa, 2008).



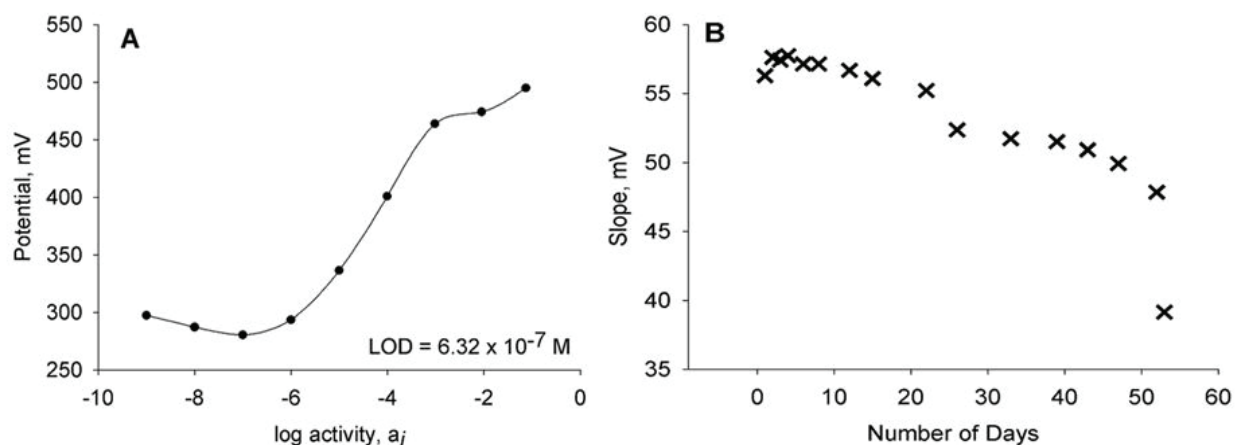
**Figure 5.** Response time and influence of solution pH on the potentiometric response of  $Ag^+$ -ISE. (A) Response time of the proposed  $Ag^+$ -ISE. The criterion of  $\pm 0.1$  mV of the final equilibrium value within 2 minutes after successive immersions of a series of  $Ag^+$  ions was used. (B) Effect of pH on the potential response of the proposed  $Ag^+$ -ISE at  $10^{-3}$  M  $Ag^+$ .

**Table 2.** Comparison of electrode performance of proposed and other published  $Ag^+$ -ISEs

Parameter	Fabricated $Ag^+$ -ISEs		
	[1]	[2]	This work
LOD	$7.0 \times 10^{-7}$ M	$6.3 \times 10^{-7}$ M	$6.32 \times 10^{-7}$ M
Linear Range	$1.7 \times 10^{-6}$ – $1.0 \times 10^{-1}$ M	$1.0 \times 10^{-6}$ – $1.0 \times 10^{-2}$ M	$1.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$ M
Slope	60.2 mV/decade	58.4 mV/decade	57.7 mV/decade
Stability	3 months	2.5 months	2 months
pH Range	3 - 7.5	4 - 6.7	3 - 9

[1] Shamsipur et al., 2002; [2] Parsa et al., 2007





**Figure 6.** (A) Linear range and detection limit of the proposed  $\text{Ag}^+$ -ISE. (B) Stability of the proposed  $\text{Ag}^+$ -ISE (all values are in mV/decade activity of ion).

Interday batch calibration ( $n = 4$  days) was done to evaluate the reproducibility for successive calibration measurements with Electrode No. E7. The average limit of detection (LOD) of the  $\text{Ag}^+$ -ISE measurement made on different days was  $5.98 \times 10^{-7} \pm 1.97 \times 10^{-7}$  M with a slope of  $57.48 \pm 0.27$  mV until 22 day of use. The proposed  $\text{Ag}^+$ -ISE was stable for 52 days without any significant decline in performance (Figure 6B), and can be re-used beyond two months storage of the dried ISE (data not shown).

These results demonstrate that the fabricated electrode has comparable performance to published ISEs for  $\text{Ag}^+$  ion determination in standard solutions.

### Analytical Application

Using photographic film wastewater, the practicability of the new  $\text{Ag}^+$ -ISE was evaluated and compared to Atomic Absorption Spectrophotometry (AAS), a standard method of analysis for metal ions. As shown in Table 3, the performance of the new  $\text{Ag}^+$ -ISE ( $\text{Ag}^+$  concentration:  $1.928 \pm 0.0491$  ppm) was comparable with AAS (Total  $\text{Ag} = 1.878 \pm 0.112$  ppm). Statistical data analyses were also done to compare the two methods using  $t$ -test (one-tailed: 2.92; two-tailed: 4.30). The results showed that two methods were not significantly different from each other (as  $t_{\text{computed}}$  is less than  $t_{\text{tabulated}}$ ) (Table 3), indicating that the fabricated  $\text{Ag}^+$ -ISE has comparable performance with the conventional AAS method.

On the practical point of view, the  $\text{Ag}^+$ -ISE method can provide faster analysis time compared to the AAS method because the former does not require any sample pre-treatment, and as such is relatively cheaper than conventional methods for the analysis of silver ions in wastewater samples. Moreover, the result of this experiment indicates that the fabricated ISE can be

**Table 3.**  $t$ -Test: Paired two sample for means (for AAS and ISE Methods)

	AAS	$\text{Ag}^+$ -ISE
Mean	1.877777778	1.928333333
Variance	0.012484883	0.002409333
Observations	3	3
Hypothesized Mean Difference		0
df		2
$t$ (computed)		-0.959740226
$t$ (tabulated)		2.91998558
$P(T \leq t)$ one-tail		0.2192302

applied for real sample analysis at trace concentration of  $\text{Ag}^+$  even to part per billion (ppb) levels. Hence the newly fabricated ISE sensor is a good alternative method *in lieu* of the AAS method as it can also be used for the quantitative determination of silver in real samples.

### CONCLUSIONS

The synthesized macrocyclic diamide, 1,15-diaza-3,4,12,13-dibenzo-5,8,11-trioxacyclooctadecane-2,14-dione or 1,3-MDA, was used as an ionophore to fabricate a PVC-based membrane  $\text{Ag}^+$  ion-selective electrode. This ISE was utilized to screen a variety of metal ions belonging to alkali, alkaline earth and transition metal ions by Separate Solution Method (SSM) and its selectivity towards silver ion was determined by Matched Potential Method (MPM). The optimization of the membrane electrode components (lipophilic additives, ionophore, PVC, plasticizer) and evaluation of its performance (detection limit, reproducibility,

response time, lifetime and selectivity) were also done. Using a univariate approach, the optimum formulation of components for the new Ag<sup>+</sup>-ISE was 47 mg PVC, 50 mg *o*-NPOE, 2 mg 1,3-MDA and 1 mg KTpCIPB. Performance-wise, the Ag<sup>+</sup>-ISE behaved Nernstially (57.75 mV/decade activity) over a wide concentration range (10<sup>-6</sup> M to 10<sup>-3</sup> M) and has low detection limit (6.32 x 10<sup>-7</sup> M). Furthermore, the proposed ISE was characterized by a good potential stability and modest lifetime, with comparable results to conventional AAS method in real samples. Because of its simplicity and practicality, this new Ag<sup>+</sup>-ISE is a promising alternative tool as an indicator electrode for potentiometric determination of Ag<sup>+</sup> ions in synthetic and real samples.

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