

The Potentiometric Analysis of Chloride Ion Using Modified Heterogeneous Chitosan Membranes

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Abstract: *The potentiometric chloride ion selectivity of a polymer membrane based on PVC and chitosan as an active material was investigated. Two dipping solutions were chosen, KCl and FeCl₃ solution. The selectivity coefficients, $K_{A,B}^{Pot}$, for some anions determined by chitosan-Cl⁻ membrane were in the sequence of $Br^- \approx I^- > HCO_3^- > NO_3^- > OH^- > SO_4^{2-} > C_2O_4^{2-}$, with values 0.03 to 0.28 ($\log K_{A,B}^{Pot} = -1.3$ to -0.55) and in the order of $CO_3^{2-} > HCO_3^- \approx F^- > ClO_3^- \approx I^- > NO_3^- \approx IO_3^- > Br^- > SO_4^{2-} > OH^-$, with values 0.01 to 0.28 ($\log K_{A,B}^{Pot} = -2.0$ to -0.55) for chitosan-Fe³⁺ membrane. The linear concentration ranges for both membranes were 1.0×10^{-4} – 1.0×10^{-1} M Cl⁻. The optimum pH were 6.5 ± 1.0 and 5.0 ± 1.0 for chitosan-Cl⁻ and chitosan-Fe³⁺, respectively. There is no significant changes in performance within 60 days for chitosan-Cl⁻ and 42 days for chitosan-Fe³⁺. The proposed membrane electrodes showed good agreement with a commercial electrode with correlation coefficient, r , 0.9560 and 0.9621 for chitosan-Cl⁻ and chitosan-Fe³⁺, respectively.*

Keywords: chloride, chitosan, heterogeneous membrane, chitosan-Cl⁻, chitosan-Fe³⁺

Abstrak: *Kepilihan ion klorida secara potensiometri suatu membran polimer berasaskan PVC dan kitosan sebagai bahan aktif telah dikaji. Dua larutan celupan dipilih, larutan KCl dan FeCl₃. Pekali kepilhan, $K_{A,B}^{Pot}$, bagi beberapa anion yang ditentukan oleh membran kitosan-Cl⁻ adalah dalam turutan $Br^- \approx I^- > HCO_3^- > NO_3^- > OH^- > SO_4^{2-} > C_2O_4^{2-}$, dengan nilai 0.03 hingga 0.28 ($\log K_{A,B}^{Pot} = -1.3$ hingga -0.55) dan dengan turutan $CO_3^{2-} > HCO_3^- \approx F^- > ClO_3^- \approx I^- > NO_3^- \approx IO_3^- > Br^- > SO_4^{2-} > OH^-$, dan nilai 0.01 hingga 0.28 ($\log K_{A,B}^{Pot} = -2.0$ hingga -0.55) bagi membran kitosan-Fe³⁺. Julat linear kepekatan bagi kedua-dua membran ialah 1.0×10^{-4} – 1.0×10^{-1} M Cl⁻. Nilai pH optimum masing-masing bagi kitosan-Cl⁻ dan kitosan-Fe³⁺ ialah 6.5 ± 1.0 dan 5.0 ± 1.0 . Tiada perubahan yang signifikan dalam prestasi selama 60 hari bagi kitosan-Cl⁻ dan 42 hari bagi kitosan-Fe³⁺. Elektrod membran yang dicadangkan menunjukkan persetujuan yang baik dengan elektrod komersial dengan pekali korelasi, r , 0.9560 dan 0.9621 bagi masing-masing kitosan-Cl⁻ dan kitosan-Fe³⁺.*

Kata kunci: klorida, kitosan, membran heterogen, kitosan -Cl⁻, kitosan-Fe³⁺

1. INTRODUCTION

The importance of chloride is immense in many areas such as in industry, agriculture and environment.¹ In addition to being used in the production of industrial chemicals, they are also useful in the production of fertilizers. The source of environmental chlorides includes leaching from several types of rocks through weathering, before it is transported into groundwater.²⁻³ Chlorides may also form from reaction of chlorine in water during power plant treatment. Consequently, this will bring about haloform reaction between hypochlorous acid and other organics such as ethanol, giving rise to the final result, chloroform, a known carcinogenic.⁴ Chloride is a well-known germicide in domestic drinking water. The permissible level of chloride recommended in drinking water is in the range of 200 to 300 mg/l.⁵⁻⁷ Chloride may cause leaf burn to sensitive crops during sprinkling and it may increase the osmotic pressure around the plant roots, which eventually prevent the water uptake.⁸ A high concentration of chloride is also blamed for metal corrosion in the domestic water piping.⁷ As such, there is a need to monitor and quantify the amount of chloride in water.

Chitosan, poly (1→4)-2-acetamido-2-deoxy-β-D-glucose is, normally, obtained from deacetylation process of amino group in chitin using strong alkali. It is normally non-porous and only easily soluble in acetic acid. Its solubility in acetic acid involves protonation of amine group in glucosamine to RNH_3^+ . Chitosan is a weak base (pKa 6.3) thus cannot be used in any acidic medium due to its solubility at lower pH. Several potentiometric studies using chitosan as membrane for ion-selective electrodes were reported.^{3,6} The previous study⁹ on the determination of Fe^{3+} ions using a heterogeneous chitosan membrane indicated serious interference from chloride. Thus, the aim of this study was to investigate on the viability of the chitosan heterogeneous membrane in the potentiometric detection of chloride ions.

2. EXPERIMENTAL

2.1 Instrument

Potentials were measured with a mV/pH meter model 720 (Orion, USA). A silver-silver chloride electrode model CRL/AgCl (Russell pH, UK) was used as the reference electrode. The pH of the sample solutions was adjusted with a conventional glass electrode No. 91-02 (Orion, USA). A commercial chloride electrode model 94-17B (Orion, USA) was used as comparison. The samples were stirred using magnetic stirrer model HI 200 M (Hanna, Singapore).

2.2 Materials

A high molecular weight polyvinyl chloride (PVC) and dioctyl phenyl phosphonate (DOPP) were obtained from Fluka Chemika (Switzerland). Tetrahydrofuran (THF) was obtained from Merck (Germany). Iron (III) chloride was obtained from BDH (England). Potassium chloride was obtained from R & M Chemicals (UK). Epoxy resin Araldite[®] was obtained from Huntsman Advanced Materials (Belgium). Chitosan powder PM100, Batch No. 01/200/121 granular size, 100 mesh, was purchased from Chito-Chem Sdn. Bhd. (Malaysia). Potassium or sodium salts of all anions used (all from Merck, Germany) were of the highest purity available and used without any further purification. Standard solutions were freshly prepared with pure water $18.2 \text{ M}\Omega\text{cm}^{-1}$ obtained from Milli-Q plus (Millipore, USA).

2.3 Heterogeneous Membrane Preparation

Chitosan powder was ground with ball mills grinder model 23917 (Pascal Engineering, England) overnight. The resultant powder was sieved to $< 50 \mu\text{m}$ size using sieve Serial No. 488677 (Retsch, Germany). A 60:40 chitosan:PVC membrane was made by first dissolving 0.06 g PVC powder in 2 ml of THF and was followed by 0.09 g of chitosan powder. Later, 10 drops of plasticizer (DOPP) was added to the mixture. The blend was stirred gently for about 5 min. The final mixture was poured into a glass ring (35 mm i.d.) on a glass plate and covered with a filter paper for a day to cure.

2.4 Electrode Fabrication

A round cut of the membrane (6 mm o.d.) was glued using Araldite[®] at one end of a borosilicate glass tube (4 mm o.d.) and was left cured for 6 h. The membrane assembly was immersed in 3.0 M KCl overnight. A 10 ml of 0.1 M KCl was added as internal filling solution. A platinum wire (Good Fellow, UK) of 45 mm length was put into filling solution to complete the electrode. The electrode assembly was stored in 20 ml 0.01 M KCl when not in use.

2.5 Electrical Measurements

The potential response was taken using the following cell scheme:



The observed potentials (emf) were measured in 20 ml of chloride solution of concentration range between $1.0 \times 10^{-6} \text{ M} - 2.0 \text{ M}$ at pH 6.5 ± 1.0 and $25.0 \pm$

2.0. The solutions were stirred constantly and the readings were taken at an interval of 30 s until they reached constant values. The emf was plotted against the logarithm of the chloride concentration. Between measurements the electrode was stored in 0.01 M KCl. The $K_{A,B}^{Pot}$ of the electrode were determined by the mixed solution method with fixed interference concentration (FIM).¹⁰

3. RESULTS AND DISCUSSION

In these experiments, the performances of chitosan as an active material in the construction of heterogeneous membranes with PVC were studied. The proposed electrodes were dipped into two different dipping solutions, 2.5 M of KCl (A) or FeCl₃ (B) solutions. The electrode B showed better Nernstian slope, -58.1 mV/dec and limit of detection, 2.511×10^{-6} M of Cl⁻ compared to electrode A, -51.9 mV/dec and 3.981×10^{-5} M of Cl⁻ (Table 1 and Fig. 1).

Table 1: Characteristic of chitosan heterogeneous membranes.

| Parameter | Membrane A | Membrane B |
|---|---|---|
| Slope, mV/dec | -51.9 | -58.1 |
| Limit of detection, M | 3.981×10^{-5} | 2.511×10^{-6} |
| Linear range, M | $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ | $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ |
| Optimum pH | 6.5 ± 1.0 | 5.0 ± 1.0 |
| Lifespan, days | 60 | 42 |
| Selectivity coefficients, $K_{A,B}^{Pot}$ | $0.03 \leq K_{A,B}^{Pot} \leq 0.28$ | $0.01 \leq K_{A,B}^{Pot} \leq 0.28$ |

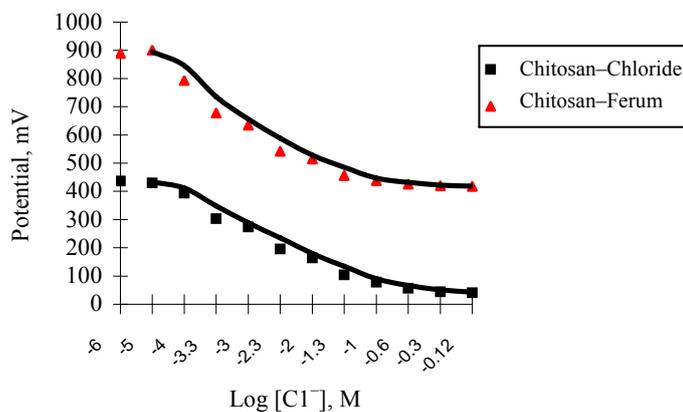


Figure 1: Calibration curves for proposed electrodes.

The rate of equilibration to achieve Donnan equilibrium, i.e. constant reading, varied from < 4 min in the more concentrated solutions (0.5 M – 1.0 M KCl) to < 30 s in dilute ones (10^{-6} M – 10^{-1} M KCl). For the very concentrated solutions of 1.5 M and 2.5 M KCl, the constant readings were obtained at 3.5 and 4 min, respectively. The faster rates of equilibration obeyed Nernst i.e. linear range. The expected ion exchange mechanisms for Donnan equilibrium to happen were as in Equations (2) and (3) for chitosan-Cl⁻ and chitosan-Fe³⁺ membranes, respectively:

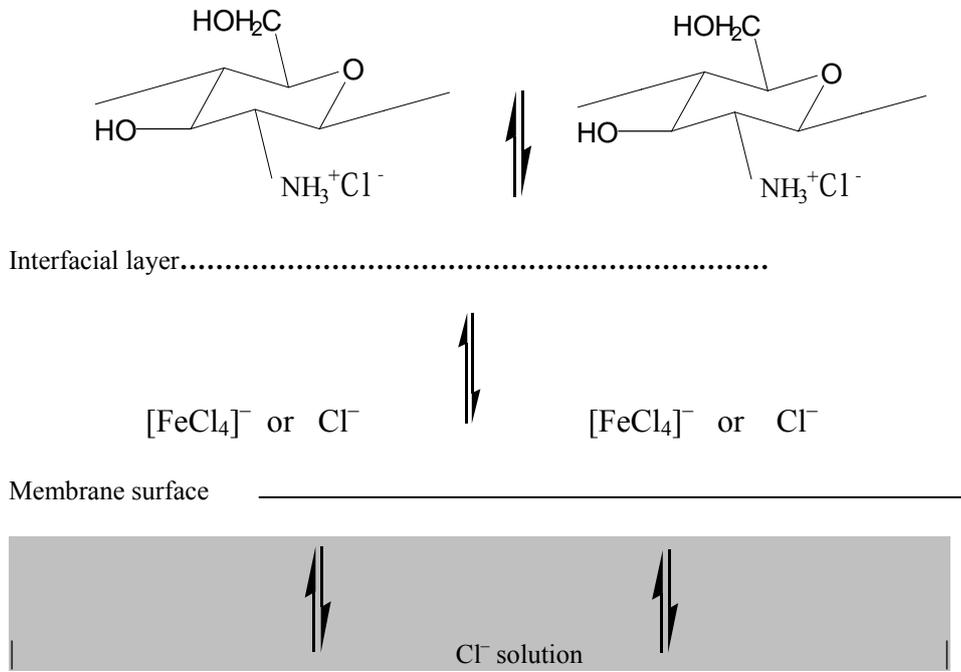
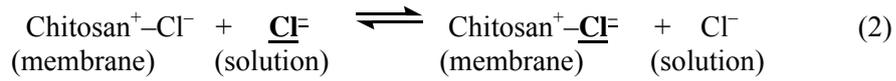


Figure 2: Illustration of ion-exchange mechanism at the surface of membrane.

The mobility to and exchange of Cl⁻ ion at cationic sites in the chitosan skeletons till equilibrium was achieved produced the Donnan potential (Fig. 2). A fast steady state was obtained in chitosan-Fe³⁺ which probably because of

thin membrane used and also elimination of swelling step during the permeation by hydrated chloride ions. The response times were almost equal for chitosan-Cl⁻ membrane. But, data acquisition was easier due to the more stable potential obtained than the chitosan-Fe³⁺ membrane. The stirring effects must also be taken into account in measuring the potential.

The emf response remained almost constant over the pH range of 4.0–8.0 for most solutions. Both heterogeneous membranes had working pH in acidic medium. The optimum pH for chitosan-Fe³⁺ and chitosan-Cl⁻ were 5.0 ± 1.0 and 6.5 ± 1.0 , respectively (Fig. 3). At higher concentrations of chlorides, variation of pH did not affect the emf response. This implied that excess of either H⁺ or OH⁻ would not interfere with Cl⁻ exchange mechanism in the membrane. For chloride concentration 0.1 M or more, the effect of pH alteration is almost nil. Study on chitosan-Fe³⁺ membrane in extreme conditions, i.e. too acidic and too basic solution, serious interference was observed from either H₃O⁺ or OH⁻ ions. H₃O⁺ ions had electrostatic repulsions with Fe³⁺ in [FeCl₄]⁻ complex; hence, interfered with the ion exchange mechanism. There was also possibility of ionic binding between H₃O⁺ ions and [FeCl₄]⁻ anionic complex. While in a very basic medium, OH⁻ ions competed with Cl⁻ ions for the exchange sites.

The selectivity of the membrane to some ions was given by the $K_{A,B}^{Pot}$ value. The higher the $K_{A,B}^{Pot}$ value examined, the higher the response of the electrode to that particular ion. This was related to the stability of the ions to form complex with ionic sites at the membrane. Ions with similar charge would

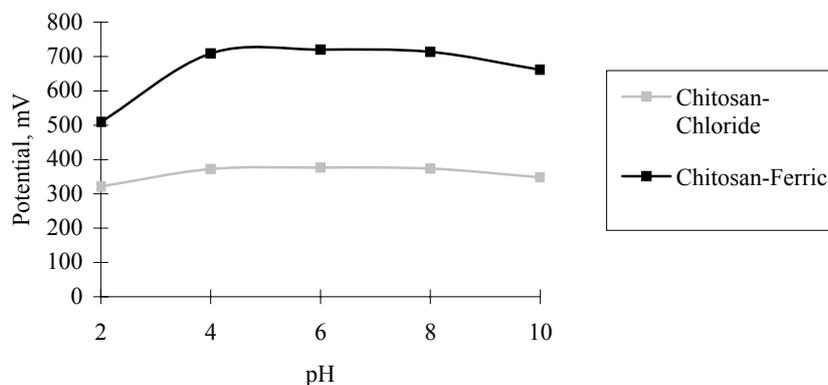


Figure 3: pH profile for chitosan-Cl⁻ and chitosan-Fe³⁺ membrane in 1.0×10^{-4} M Cl⁻.

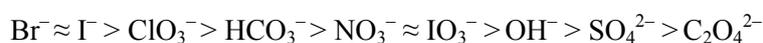
be effectively repelled from the membrane surface. Size of the ions was another factor that influenced the mobility of the ions to the membrane surface. The smaller the ions the more easily they were in their mobility to the membrane surface than bulky ions.

The 1.0×10^{-2} M concentration of interfering ions, B , used in these experiments was high. Both membrane electrodes showed poor selectivity towards primary ion, A , examined from the decrease of Nernst slopes from -58.1 mV/dec to -6.54 mV/dec and -51.9 mV/dec to -14.78 mV/dec for chitosan- Fe^{3+} and chitosan- Cl^- ISE, respectively. The emf responses have also decreased, especially, at lower concentrations of chloride (Table 2). The $K_{A,B}^{Pot}$ ranges were 0.03 to 0.28 ($\text{Log } K_{A,B}^{Pot} = -1.3$ to -0.55) and 0.01 to 0.28 ($\text{Log } K_{A,B}^{Pot} = -2.0$ to -0.55) for the chitosan- Cl^- and chitosan- Fe^{3+} , respectively.

Table 2: The selectivity coefficients, $K_{A,B}^{Pot}$ of proposed membranes to some interfering ions. [P, slope (mV/dec); Q, limit of detection (M); R, linear ranges (M); S, Selectivity coefficients ($K_{A,B}^{Pot}$); B, Interfering ions].

| B | Chitosan- Cl^- | | | | | Chitosan- Fe^{3+} | | | |
|-----------------------------|-------------------------|-----------------------|---------------------------------------|------|--------|----------------------------|---------------------------------------|------|--|
| | P | Q | R | S | P | Q | R | S | |
| CO_3^{2-} | - | - | - | - | -6.54 | 2.82×10^{-3} | $1 \times 10^{-2} - 1 \times 10^{-4}$ | 0.28 | |
| $\text{C}_2\text{O}_4^{2-}$ | -21.9 | 2.95×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.03 | - | - | - | - | |
| NO_3^- | -23.3 | 1.41×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.14 | -21.04 | 1.41×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.14 | |
| ClO_3^- | -21.8 | 2.24×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.22 | -20.41 | 1.58×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.16 | |
| HCO_3^- | -30.0 | 1.78×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.18 | -20.11 | 2.51×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.25 | |
| Br^- | -25.1 | 2.82×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.28 | -22.07 | 1.12×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.11 | |
| IO_3^- | -30.8 | 1.41×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.14 | -29.2 | 1.41×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.14 | |
| OH^- | -14.8 | 7.08×10^{-4} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.08 | -27.13 | 1.12×10^{-4} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.01 | |
| SO_4^{2-} | -19.5 | 5.01×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.05 | -11.99 | 1.59×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.02 | |
| I^- | -22.6 | 2.75×10^{-3} | $1 \times 10^{-1} - 5 \times 10^{-3}$ | 0.28 | -20.51 | 1.59×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.16 | |
| F^- | - | - | - | - | -25.23 | 2.52×10^{-3} | $1 \times 10^{-1} - 1 \times 10^{-3}$ | 0.25 | |

For chitosan- Cl^- , the $K_{A,B}^{Pot}$ were in the order of:



While for chitosan-Fe³⁺, the $K_{A,B}^{Pot}$ were in the order of:



It was interesting to note that for chitosan-Fe³⁺ membrane, other halide ions, Br⁻ and I⁻, did only interfere slightly as opposed to other non-halides. The divalent ions tested did not interfere. Table 2 also showed that CO₃²⁻, HCO₃⁻ and F⁻ interfered more to the response compared to other ions. The lifespans were 42 and 60 days for chitosan-Fe³⁺ and chitosan-Cl⁻ membrane, respectively (Fig. 4).

The membrane electrodes were applied to test the concentration of Cl⁻ in five samples, *viz.* mineral water, tap water, sea water, soybean and oranges (Table 3). Results showed significant difference for Cl⁻ concentration in mineral water and tap water detected by chitosan-Cl⁻ and chitosan-Fe³⁺ compared to the commercial electrode. For soybean and oranges, the solutions have already had natural buffer systems in, which probably contributed to similar result as the commercial membrane electrode.

Table 4 shows the percentage of recovery were more than 84% for chitosan-Cl⁻ and more than 90.7% for chitosan-Fe³⁺. Degree of correlation, *r*, between chitosan-Cl⁻ and the commercial electrodes was in the ranges of 0.426–1.006. The *r* for chitosan-Fe³⁺ membrane electrode was in the ranges of 0.686–0.989.

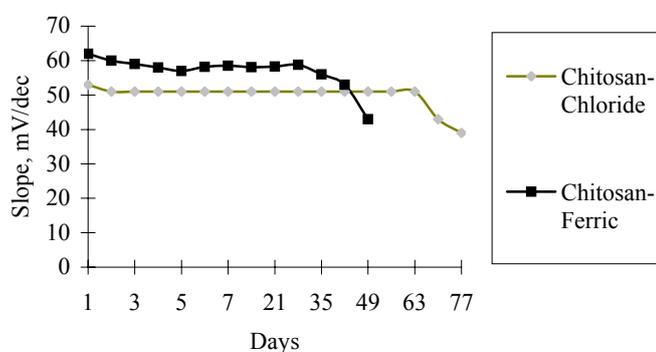


Figure 4: The lifespan for proposed membrane electrodes.

Table 3: The analyses of Cl^- in real samples using proposed and commercial membrane electrodes. ($n = 3$)

| Samples | Chitosan- Cl^- (mM) | Chitosan- Fe^{3+} (mM) | Commercial (mM) |
|---------------|------------------------------|---------------------------------|---------------------|
| Mineral water | 0.931 ± 0.119 | 0.9084 ± 0.001 | 0.121 ± 0.008 |
| Tap water | 0.662 ± 0.012 | 0.6628 ± 0.0002 | 0.378 ± 0.002 |
| Sea water | 171.700 ± 0.386 | 97.0000 ± 0.133 | 179.700 ± 0.386 |
| Soybean | 2.068 ± 0.258 | 2.1400 ± 0.272 | 2.070 ± 0.257 |
| Oranges | 9.441 ± 0.668 | 8.6610 ± 0.691 | 9.400 ± 0.668 |

Table 4: Validation of proposed membrane electrodes. (r = correlation coefficient; R^2 = regression of coefficient)

| Samples | Chitosan- Cl^- | | | Chitosan- Fe^{3+} | | |
|------------------------|-------------------------|--------|------------------------|----------------------------|--------|------------------------|
| | r | R^2 | Range of % recovery | r | R^2 | Range of % recovery |
| Cl^- solution | 0.956 | 0.9974 | $(97.0-100.2) \pm 1.0$ | 0.962 | 0.9982 | $(95.0-100.5) \pm 1.3$ |
| Tap water | 0.577 | 0.9543 | $(96.8-100.6) \pm 2.0$ | 0.796 | 0.9919 | $(98.1-106.0) \pm 4.1$ |
| Sea water | 1.006 | 0.9993 | $(86.1-104.6) \pm 5.8$ | 0.989 | 0.9994 | $(96.9-104.7) \pm 3.9$ |
| Mineral water | 0.494 | 0.9794 | $(93.7-101.6) \pm 4.3$ | 0.686 | 0.9719 | $(98.4-106.2) \pm 4.1$ |
| Orange | 0.684 | 0.9776 | $(84.7-100.1) \pm 6.0$ | 0.847 | 0.9999 | $(96.3-106.8) \pm 5.3$ |
| Soybean | 0.426 | 0.9898 | $(97.8-100.1) \pm 1.2$ | 0.907 | 0.9999 | $(90.7-100.0) \pm 4.9$ |

4. CONCLUSION

Both chitosan- Cl^- and chitosan- Fe^{3+} membrane electrodes were capable of measuring Cl^- in spite of interferences from other halides. The latter should not be present if chitosan- Cl^- was used. The chitosan- Fe^{3+} , however, was more likely to be interfered by carbonate and bicarbonate. The indirect determination of Cl^- by chitosan- Fe^{3+} membrane gave higher response than the chitosan- Cl^- in the analysis of Cl^- in terms of stability during measurements, near Nernstian slope and degree of correlation with the commercial membrane electrode. This, however, would be minimized through standard addition method and application of the total ionic strength adjustment buffer (TISAB) solution.

5. ACKNOWLEDGEMENT

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