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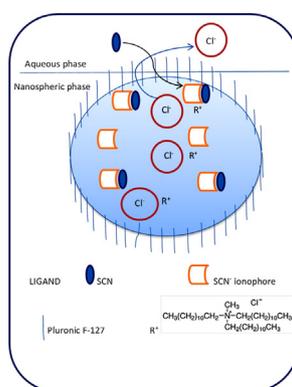
Development of ionophore-based nanosphere emulsion incorporating ion-exchanger for complexometric titration of thiocyanate anion



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GRAPHICAL ABSTRACT



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ABSTRACT

Ionophore-based ion-exchange nanosphere emulsion was prepared and tested for the determination of thiocyanate. The emulsified nanosphere contained the cationic additive tridodecylmethyl ammonium chloride (TDMAC), the plasticizer, and the ionophore Mn(III)-salophen or Mn(III)-salen. This emulsion was used as titrating agent for thiocyanate complexation with ionophores, which could be transduced using an ion-selective electrode (ISE) as an indicator electrode for the end point detection. The method showed no need for pH control and reliable selectivity, as thiocyanate could be determined in presence of other interfering ions with high accuracy. As well, the emulsion was stable and could be used for approximately couple of weeks. The developed emulsion could be used for the determination of thiocyanate in human saliva with standard deviation <4%. In sum, the proposed method could be used as an alternative for the argentometric titration and would open new avenues for the determination of neutral, anionic, and cationic species without necessity for water soluble ligands or pH control.

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Introduction

Complexometric titration is a classic method that could be used for the determination of plethora of metal cations using different ligands or chelating agents [1]. These ligands form so stable complexes with the metal cations and the end point can be detected easily using visual indicators. However, the absence of the suitable chelating agent that can form stable complex with anionic species

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limits the application of this valuable method for anion determination [1]. Argentometric titrations could overcome this problem using different methods (Mohr, Fajan and Volhard) [2]. However, these methods still suffer from the limited applicability to certain number of anions (halides, cyanide, phosphate, sulphide, and thiocyanate), the necessity for pH control, and formation of the precipitate that may hinder the visual detection of the end point [2].

On the other hand, ion-selective electrodes (ISEs) are one of the simplest instrumental techniques that offer several benefits, such as low cost, short response time, ease of construction, high selectivity, and on-line monitoring [3]. The most important component of the ISE is the ionophore that controls the selectivity of electrode via molecular recognition between the ionophore and the analyte [3,4]. So far, very large numbers of ionophores were used for the determination of the different anionic species [3–6] to overcome the problem of complexometric titrations. Potentiometric titration is a derivative of ISEs that could be applied for the determination of different species [6,7], easy to perform, cost-effective, and applicable when used in turbid solutions.

The advantages of complexometric titration, ISEs, and potentiometric titration could be joined in a powerful technique named complexometric titration using ionophore-based ion-exchange emulsion. This method was first reported by Zhai et al. for the determination of metal cations, Pb^{2+} , and Ca^{2+} , using ionophore-based nanosphere emulsion [8]. The aqueous analyte concentrations of Pb^{2+} or Ca^{2+} were titrated against ionophore-based ion-exchange emulsions as titrant. The lipophilic ion-exchanger extracted the analyte ions from the aqueous phase to the lipophilic nanosphere phase to be complexed by the specific ionophore. This depletion in the concentration of the aqueous cation caused a decrease in the potential reading of the indicator electrode. The amount of extracted ions was controlled by the ion-exchanger amount, where the ionophore was responsible for controlling selectivity [8]. Schwarzenbach conditions for complexometric titration were satisfactory, as the small size of the nanosphere <100 nm, ensures rapid complexation reaction between ionophore and analyte ion with definite stoichiometry and high formation constant [2,3]. Later, the same group could apply this method for the determination of perchlorate [9]. However, this work lacked the selectivity as the emulsion was only ion-exchanger based.

Therefore, this work was designed to report the use of ionophore-based ion-exchange emulsion for the determination of an anion, thiocyanate. This enable us to move the complexometric titration from the homogenous aqueous phase to the heterogenous aqueous/organic phases, which allow the possibility of complexing different anions by different ionophores. Thiocyanate was taken as an example, where this approach can be applied for the different anions using the suitable ionophore.

Experimental

Reagents and solutions

All chemicals were of analytical grade. Pluronic F-127 (F127), 2-nitrophenyl octyl ether (*o*-NPOE), tetrahydrofuran (THF), sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), tridodecylmethylammonium chloride (TDMAC), Mn(III)-salen (Fig. 1), and high molecular weight poly (vinyl-chloride) (PVC) ($M_w = 43,000$) were obtained from Sigma-Aldrich (Munich, Germany). Potassium thiocyanate (KSCN), Silver nitrate ($AgNO_3$), glacial acetic acid, and sodium acetate were obtained from ADWIC (Cairo, Egypt). Mn(III)-salophen ionophore (Fig. 1) was prepared as reported before [6].

Double distilled water was used throughout the experimental work for the preparation of the buffer and different solutions. $10^{-1} \text{ mol L}^{-1}$ KSCN or KI stock solutions were prepared by dissolving the exact weight in double distilled water and the lower concentration solutions were prepared by appropriate dilutions. Acetate buffer was prepared as described elsewhere [10,11]. Briefly, $5.0 \times 10^{-2} \text{ mol L}^{-1}$ sodium acetate was prepared by dissolving the exact weight in 240 mL double distilled water followed by addition of drops of glacial acetic acid to adjust the pH at 4.5 and mass up with water to 250 mL. This buffer could be used later for the preparation of thiocyanate solutions.

Saliva samples were collected from a healthy person (corresponding author) and treated as reported before [6]. The collected saliva samples (two) transferred to centrifugation tubes and centrifugated at 6000 rpm for ten min. From the resulting clear solutions, volume of 250 μL was pipetted into a 25 mL volumetric flask. This solution was used in titration against Mn(III)-salophen-based emulsion for the determination of its thiocyanate content; the experiment was repeated thrice. The results were compared with that obtained from the potentiometry using ISE [6]. Different amounts of SCN^- and 1 mL urine of the corresponding author were transferred to 25 mL measuring flask and adjusted to the mark with water [5]. These solutions were subjected to the potentiometric titration using Mn(III)-salophen emulsion and experiment was repeated three times.

Preparation of thiocyanate-selective emulsion

For Mn(III)-salophen-based emulsion, 2.24 mg of ionophore, 1.24 mg of TDMAC (68% (mole ratio of ion-exchanger/ionophore)), 8.0 mg of *o*-NPOE, and 3.0 mg of F127 were dissolved in 2.0 mL of THF to form a homogeneous solution. Aliquot of 0.5 mL THF solution was pipetted and 3 mL double distilled water was injected, then vortexing at 1000 rpm. Compressed air was blown on the surface for 30 min to remove THF. For Mn(III)-salen emulsion, 10.3 mg of the ionophore, 0.63 mg of TDMAC (6.8% (mole ratio of ion-exchanger/ionophore)), 6.08 mg of *o*-NPOE, and 2.48 mg of F127 were dissolved in 2.0 mL of THF, followed by the same procedures above [8,9].

Membranes and electrodes

The thiocyanate-selective membrane was prepared by dissolving the mixture composed of 16.5 mmol kg^{-1} ionophore, 6.9 mmol kg^{-1} NaTFPB, 63.1 wt% *o*-NPOE, and 33.5 wt% PVC in 1.5 mL THF. The cocktail solution was then poured into a glass ring (22 mm in diameter) placed on a glass slide and dried overnight at room temperature under a dust-free environment. Proper part of the membrane was punched and glued to a polished end of a PVC tube using PVC/THF slurry. An inner filling solution of $10^{-2} \text{ mol L}^{-1}$ thiocyanate was used and then the electrodes were conditioned for 24 h in the same solution, pending uses as an indicator electrode [6].

Instrumentations and measurements

For potentiometric titrations, ionophore-based emulsions as titrating agents were titrated against 4.0×10^{-5} , 1.0×10^{-5} , and $1.0 \times 10^{-4} \text{ mol L}^{-1}$ KSCN aqueous and buffered analytes, and the thiocyanate-selective electrode as endpoint detector. In case of selectivity measurement, the analyte solution contained $2.5 \times 10^{-5} \text{ mol L}^{-1} SCN^-$ and $1.1 \times 10^{-5} \text{ mol L}^{-1} I^-$ was titrated against Mn(III)-salophen titrant.

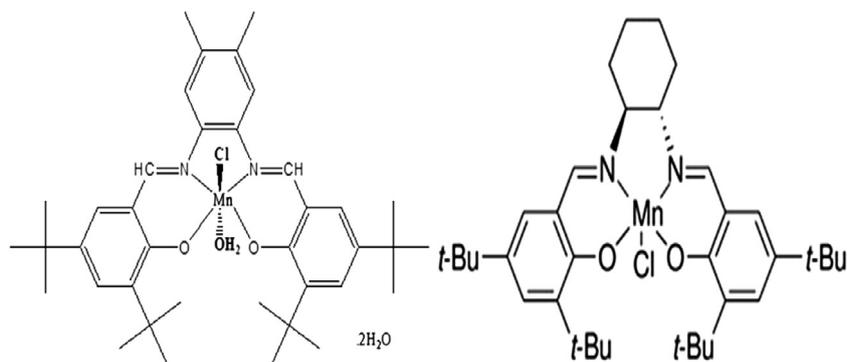


Fig. 1. Structure of Mn(III)-salophen (left) and Mn(III)-salen (right) ionophores.

Results and discussion

Response mechanism

Complexometric titration using nanosphere emulsion was proven to be efficient alternative for the classic complexometric titration because of its ability to use water insoluble ligands, absence of necessity for pH control, and many other advantages [8,9]. Efficiency of the method is acquired from verifying the conditions of Schwarzenbach for ideal complexometric titration [2,3]. The principal of operation is identical to that shown by Zhai et al. [8] with inversion of charge of analyte and ion-exchanger. Fig. 2 shows that the plasticizer droplets are surrounded by the surfactant (F127) and the emulsion core (contains these droplets) contains the dissolved TDMAC and ionophore. The counter ion of TDMAC, chloride,

is exchanged with thiocyanate, which is then complexed with the lipophilic ionophore. A stoichiometric complex of defined ratios (1:1) is formed between the thiocyanate and the lipophilic ionophore Mn(III)-salophen [6]. The stability of this complex was measured using sandwich membrane method (i.e. the ion-exchange reaction is considered as the reference or the zero-point for the determination of the formation constant) and found to be very high, $\beta = 10^{14.1}$. In case of the other ionophore of similar structure, Mn(III)-salen, it is expected to exhibit same characters. While the ion-exchanger controls the amount of the extracted thiocyanate from the aqueous phase to the emulsion and can be used solely [8], the ionophore controls the selective binding of the target anion and exhibits sharp end point. As the ion-exchanger is in lower amount to control the reaction ratio, it might not be important to estimate the ionophore: thiocyanate ratio.

For fulfilling the conditions of Schwarzenbach, very small size of nanospherical particles, <100 nm [8,9,12], ensures rapid phase transfer and so achieve the first requirement. The stoichiometry is well-known from the potentiometric study [6], which achieve the second requirement. The formed complex is of very high stability, and this stability is increased using excess amount of the ionophore within the emulsion, to prevent reverse reaction, which achieve the third requirement reported for complexing agents.

In the complexometric titrations, each ionophore was used as a titrating agent and the end point was detected using potentiometric thiocyanate-selective electrode. A relation can be obtained between the micromoles of TDMAC added in the titrant and the measured potential, which can be converted to pSCN using Nernst equation. For sharp end point detection, first derivative can be used, Fig. 3.

Two different concentrations of thiocyanate were used as analytes for testing the ionophore-based emulsions (Fig. 3). The end point was sharp in case of Mn(III)-salophen ionophore (graphs 1, 2 in Fig. 3), due to higher lipophilicity and stability constant for Mn(III)-salophen over Mn(III)-salen [6]. Additionally, the results showed very good agreement between the experimental end points and the theoretical equivalence points, as indicated by the vertical lines. The relative error was about less than 4%.

Effect of pH

One of the most important disadvantages in the argentometric titration is the importance of the pH control. In Volhard method, acidic condition is a prerequisite for the end point detection [2,3]. Moreover, the low solubility of silver thiocyanate was considered as another pitfall. To overcome these limitations, the titrations in this work were repeated in buffered thiocyanate solution using acetate buffer of pH 4.5. Notably, the end point in the buffered solution (Fig. 4) was the same as that of the unbuffered solutions

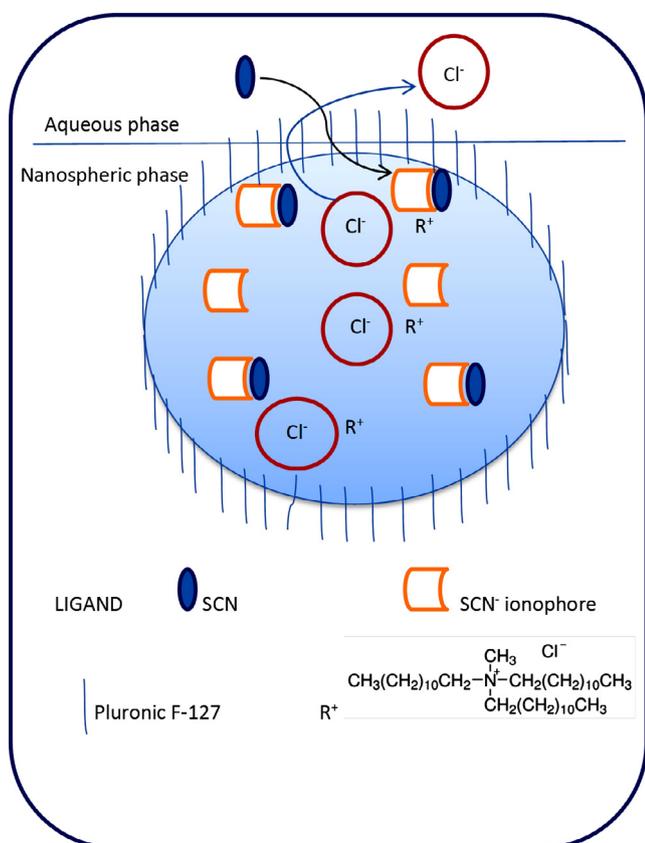


Fig. 2. Scheme for the response mechanism of the ionophore-based ion-exchange nanosphere.

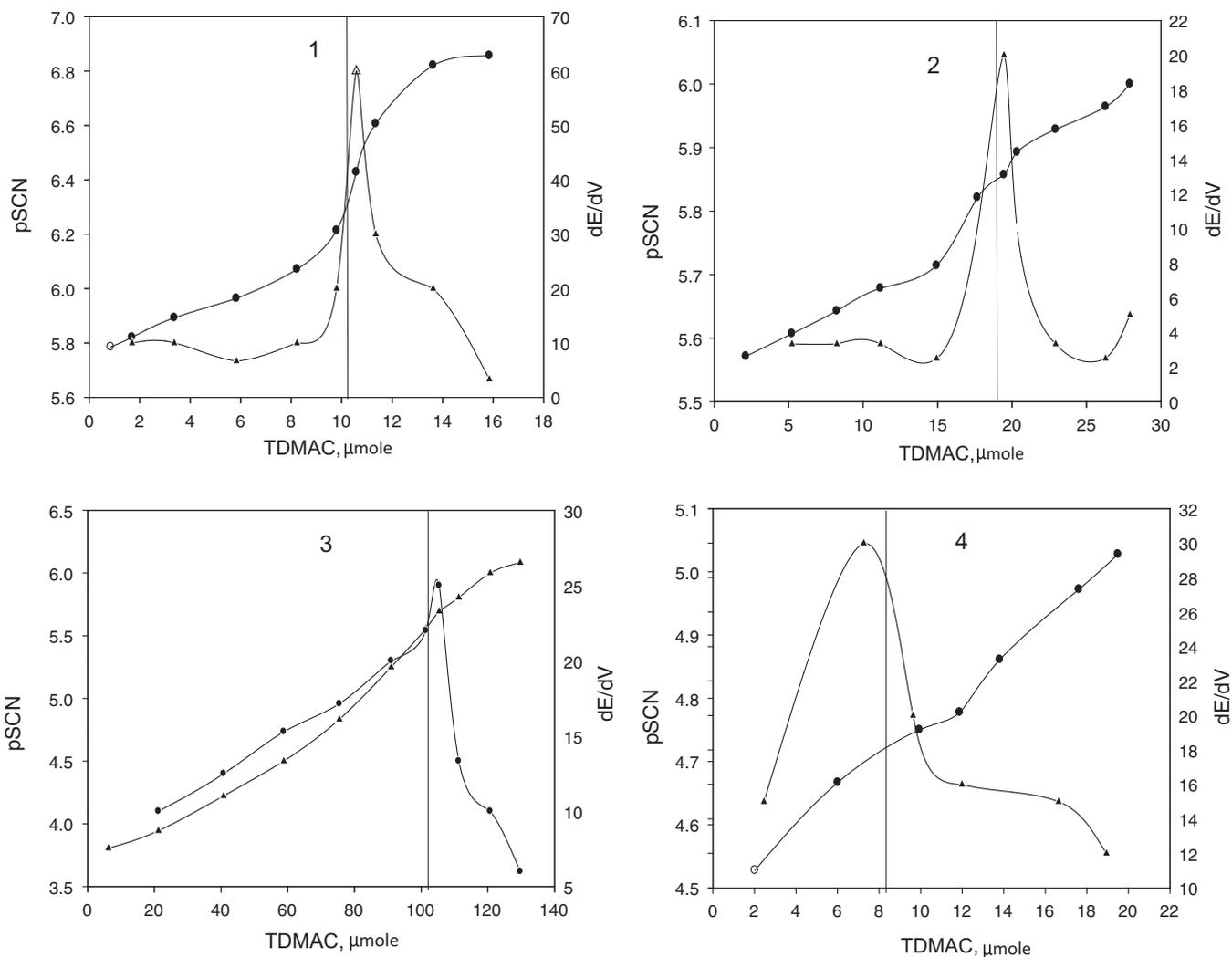


Fig. 3. (●) Potentiometric titration and (▲) first derivative plots for (1) 1.0×10^{-5} and (2) $4.0 \times 10^{-5} \text{ mol L}^{-1}$ thiocyanate using Mn(III)-salophen, (3) 1.0×10^{-5} , and (4) $1.0 \times 10^{-4} \text{ mol L}^{-1}$ thiocyanate using Mn(III)-salen ionophores in unbuffered water. Vertical lines indicate the theoretical end point.

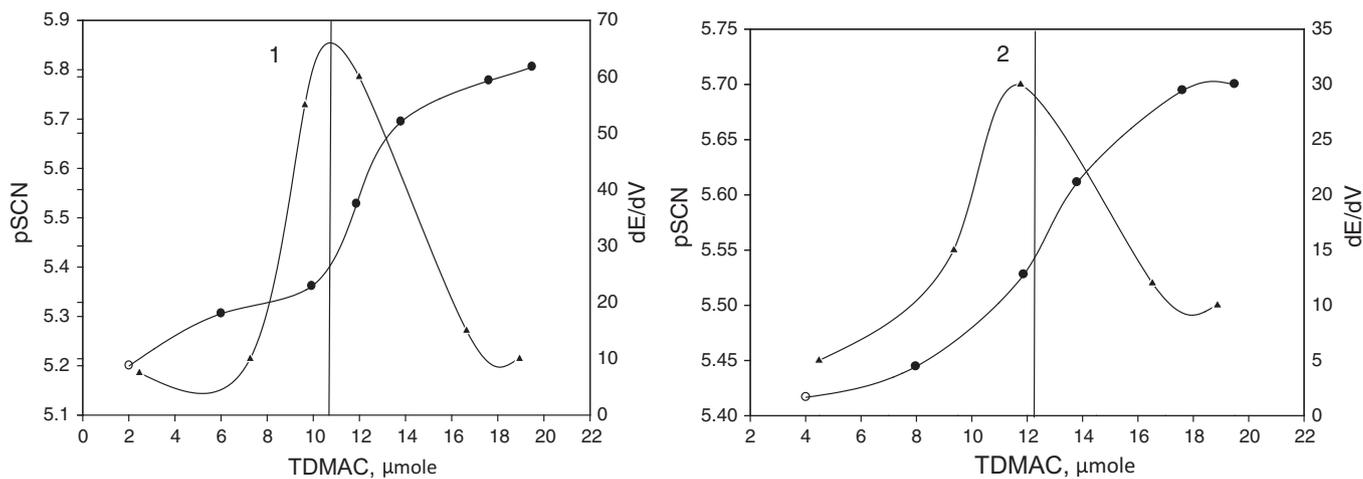


Fig. 4. (●) Potentiometric titration and (▲) first derivative plots for $1 \times 10^{-5} \text{ M}$ thiocyanate using (1) Mn(III)-salen and (2) Mn(III)-salophen ionophores in acetate buffer pH 4.5. Vertical lines indicate the theoretical end point.

(Fig. 3(1) and (3)). Therefore, there is no need to work on controlled pH.

Effect of interfering ions

The titration was carried out in a solution that contained both the thiocyanate and iodide ions. Fig. 5 shows that both the primary ion (2nd end point) and interfering ion (1st end point) were determined using the emulsion. This is expected because the ion-exchanger TDMAC is responsible for the extraction of any anion from the aqueous phase to the surface of the nanosphere [9]. However, the presence of the Mn(III)-salophen ionophore causes sharper end point in thiocyanate more than iodide, which is clear in both the titration curve and the first derivative curve, Fig. 5.

Any other interfering ion is expected to demonstrate similar behavior to that of iodide due to the presence of the ion-exchanger. The role of the ionophore is to clarify and exhibit sharp end point.

Applications

The method was used to determine the concentration of thiocyanate in human saliva and spiked urine samples using emulsion containing the salophen ionophore. The results were compared to that obtained by ISE [6]. The results in Table 1 have shown high recovery values and high reproducibility as ensured by low standard deviation values. The student *t*-test was performed to ensure the method validity, and it shows lower calculated values than theoretical values (Table 1).

Another application was the comparative potentiometric titration performed between thiocyanate analyte against silver nitrate or ionophore-based emulsion (Fig. 6). Both end points of silver nitrate and ionophore-based emulsion exhibited relative error against theoretical end point <1%, which ensures the success of this method for different applications.

Conclusions

Complexometric titration using the ionophore-based ion-exchange emulsion for determining thiocyanate, as a proof of concept, is reported. The method depends on heterogeneous ion exchange equilibria followed by strong complexation of the analyte to the ionophore. End point can be detected easily from

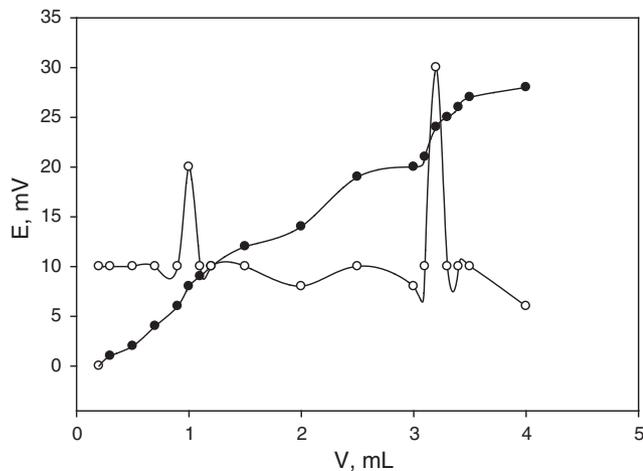


Fig. 5. (●) Potentiometric titration and (○) first derivative plots for 2.5×10^{-5} M thiocyanate and 1.1×10^{-5} M iodide using Mn(III)-salophen ionophores in acetate buffer pH 4.5.

Table 1

Determination of thiocyanate in saliva and spiked urine samples using the emulsion titration and reference method [6].

	Emulsion titration	<i>t</i> -test ^a	Ref. [6]
Saliva	$34.1 \pm 0.1 \mu\text{mole L}^{-1}$	1.0	$34.0 \pm 0.2 \mu\text{mole L}^{-1}$
Spiked urine	$23.0 \pm 0.2 \mu\text{mole L}^{-1}$	1.0	$23.2 \pm 0.1 \mu\text{mole L}^{-1}$

^a Theoretical *t*-value (0.05, 3) is 3.18.

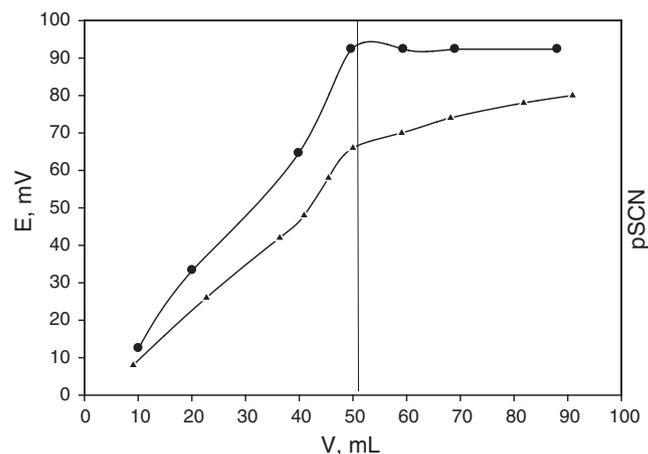


Fig. 6. Potentiometric titrations for aqueous solutions of thiocyanate using (●) 10^{-2} M AgNO_3 and (▲) Mn(III)-salen-based emulsion. Vertical line indicates the theoretical end point.

the first derivative plot. The method could be applied for determination of thiocyanate in saliva and spiked urine samples with no need for pH control. This method opens new avenues for using the titration in determining very low concentrations (micro molar) of anionic, cationic, and even neutral species using the suitable ionophore without the need for coloring indicators or pH control. Although the use of some ionophores may cause high cost of analysis, but the large library of different selective ionophores can overcome this problem.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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