

# APPLICATION OF HOME MADE $\text{Ag}_2\text{S}$ ELECTRODE IN ALKALINE MEDIA

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**Abstract:** Home made silver sulphide ion selective electrode was prepared and applied for argentometric titration in alkaline media for the determination of thiamine hydrochloride. The amount of thiamine hydrochloride estimated from titration of ionisable chloride with silver nitrate was found to be 637 mg/g of the vitamin  $\text{B}_1$  tablet. This result is in agreement with the value obtained from ion chromatographic (IC) and cyclic voltammetric (CV) techniques. In presence of chloride from other sources, these techniques fail, but thiamine in pharmaceutical preparation, however, can be determined by potentiometric titration in highly alkaline medium using silver- sulphide membrane electrode with silver nitrate solution at which there is no interference due to the presence of chloride from other sources. The results showed that home made silver- sulphide electrode can be used as an indicator electrode for the potentiometric determination of thiamine in pharmaceutical preparation.

**Keywords:** Silver sulphide electrode; Potentiometric titration; Thiamine; Vitamin  $\text{B}_1$ .

## INTRODUCTION

Soluble halides can readily be estimated by argentometric titrations with standard silver nitrate solution using ion selective electrode (ISE). ISE is an excellent tool to detect the end point in titrimetric analysis. The development and application of ISEs is an exciting and expanding area of analytical research<sup>1</sup>. It is obvious that the ability to make direct or indirect measurements in complex samples without concern about sample color or turbidity and the fact that such measurements require relatively inexpensive equipment make ISE based technique attractive to scientists in many disciplines. Potentiometric application of ISEs has been used in the control of pharmaceutical products and it has been considered as a successful alternative to the conventional analytical techniques<sup>2-3</sup>.

In this work, ISE with precipitate based silver sulphide electrode have been prepared to study the argentometric titration in alkaline media. Preparation and characterization of electrodes in terms of Nernstian response, response time, detection limit, and selectivity coefficients were discussed elsewhere<sup>4-8</sup>.

The major component of commercial vitamin  $\text{B}_1$  tablet is thiamine hydrochloride. It is available in the form of colloidal dispersion, capsule or tablets in pharmaceutical products to supplement the vitamin  $\text{B}_1$  deficiency. The determination of

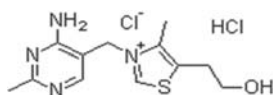
thiamine hydrochloride is clinically important. The content of thiamine, in pharmaceutical preparation can be determined by a number of methods such as gravimetric methods<sup>9</sup>, titrimetric methods<sup>2-3</sup>, thin layer chromatography<sup>10</sup>, gas chromatography<sup>11</sup>, capillary electrophoresis<sup>12</sup>, high performance liquid chromatography<sup>13</sup>, fluoremetry<sup>14</sup> and spectrophotometry<sup>15-16</sup>, electrochemical analysis method<sup>17-22</sup>. These days, ISEs have been increasingly used in the different fields including pharmaceutical analysis, and can be used for quantitative estimation of thiamine hydrochloride in pharmaceutical preparation. The present paper describes a simple method of potentiometric determination of thiamine hydrochloride in pharmaceutical preparation using silver sulphide electrode and the results are compared with ion chromatographic (IC) and cyclic voltammetric (CV) measurements.

## EXPERIMENTAL

### Reagents

All reagents were of analytical grade. Silver nitrate, sodium chloride and thiamine hydrochloride were purchased from Sigma Aldrich. Molecular structure of thiamine hydrochloride is shown in **Fig (1)**. Commercial tablets containing thiamine were obtained from local drug store. The pure powders and pulverised tablets were dried at 60°C for 2 hours under vacuum. All aqueous solutions were prepared with distilled water.

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**Figure 1:** molecular structure of thiamine hydrochloride

### Sample preparation

Tablets were pulverised to fine powder and vacuum dried. Then the required amount of powder was dissolved into minimum amount (about 20 mL) of water. Thus obtained solution was filtered into a 100 ml volumetric flask and made up to the mark with distilled water.

### Instrumentation

Potentials were measured by using OSAW- digital potentiometer (India) relative to a silver-silver chloride (sat) reference electrode. The potentiometric measurements were made with the following electrochemical cell Ag/AgCl/ KCl (sat)//sample solution/ Ag<sub>2</sub>S/ Ag.

Dionex Corporation, USA, GP 50 gradient pump having LC 25 chromatography oven was used in ion chromatographic method. Column used was Ion Pac AS4A-Sc Dionex having 4mm i.d. x 250 mm with precolumn AG 4A-Sc. Electrochemical suppressor used was ASRS ultra II 4mm. The detector was a conductometric detector ED 40. Samples were introduced into the analytical column by direct injection with a sample loop. The sample injection volume was 10 µL having flow rate of 1.5 µL/min. Eluent used was a mixture of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in the concentration range of 1.7x10<sup>-3</sup> M and 1.8x10<sup>-3</sup> M respectively. The amount of chloride in authentic thiamine hydrochloride sample was estimated by making calibration curve in the range of 1x10<sup>-4</sup> & 1x10<sup>-5</sup> M.

In cyclic voltammetric method, a silver disk was used as working electrode, saturated calomel as reference electrode and a cylindrical platinum as counter electrode immersed into a mixture of tetraethyl ammonium tetrafluoroborate (TEATFB) and thiamine hydrochloride (vitamin B<sub>1</sub>). The amount of chloride in thiamine hydrochloride (vitamin B<sub>1</sub>) was estimated by using a calibration curve for chloride ion. A blank calibration curve was obtained in the range of 1 mM to 50 mM HCl. For estimating the amount of chloride in thiamine hydrochloride (vitamin B<sub>1</sub>), above mentioned HCl solution was added into thiamine hydrochloride (vitamin B<sub>1</sub>) sample solution. Cyclic voltammogram was recorded from 500 to -500 mV at a scan rate of 100 mV/sec. All measurements were carried out at 25°C in argon environment.

### Procedure of argentometric titration

The potentiometric titration of 10 mL of (0.01M) NaCl with (0.01M) AgNO<sub>3</sub> solution was carried out to estimate the amount of Cl<sup>-</sup> in solution. The titration was also carried out in presence of different concentrations of alkaline NaOH.

### Determination of thiamine in pharmaceutical preparations (vitamin B<sub>1</sub> tablet)

In ISE method, 10 mL of vitamin B<sub>1</sub> sample solution was transferred in a beaker by a volumetric pipette. The electrode in conjunction with the reference electrode was immersed in

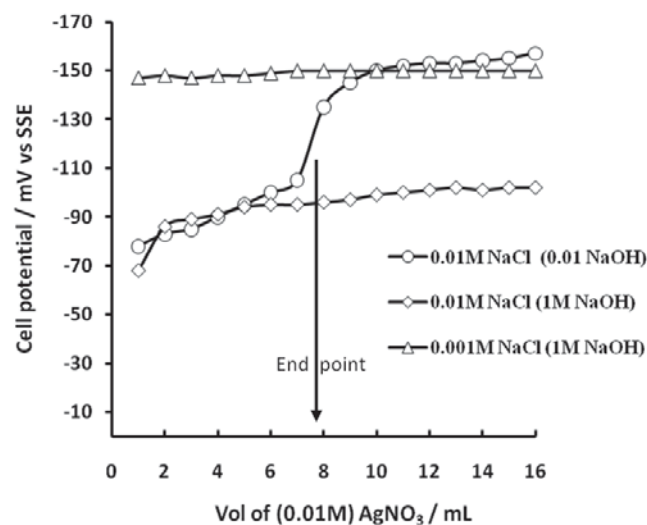
it. The solution was titrated with a 0.01M silver nitrate. The end point of the titration was determined potentiometrically. The titration was also carried out in highly alkaline (> 0.01 M NaOH) medium.

## RESULTS AND DISCUSSION

### Argentometric titration using Ag<sub>2</sub>S electrode

The silver sulphide electrode gives potentiometric response to both silver and sulphide ions. A linear response with a slope of 59.8 mV/decade change in concentration was observed in the concentration range from 10<sup>-1</sup>M to 10<sup>-6</sup>M of silver ion, followed by a non linear region at lower concentrations. Similarly, the Ag<sub>2</sub>S electrode was also found to be sensitive to the sulphide ion. The change in slope per decade change in sulphide ion concentration was found to be 30 mV which is the expected value for a divalent ion. The results are presented in our previous papers [4-8]. To test the usefulness of Ag<sub>2</sub>S ISE as an end point indicator in alkaline medium, argentometric titration of AgNO<sub>3</sub> with NaCl was carried out at varying concentration of NaOH solution. In this titration, 10 mL of 0.01 M NaCl solution was titrated with 0.01 M AgNO<sub>3</sub> while the concentration of NaOH was changed from 10<sup>-2</sup> M to 1 M. It is interesting to note that when sodium chloride solution is titrated with silver nitrate in 1000 times higher concentration of sodium hydroxide, the inflation point was diminished.

In **Fig (2)**, when NaOH concentration is equal to chloride concentration, a clear inflation was observed in between 7 and 8 mL of AgNO<sub>3</sub>, but when NaOH concentration was increased by 100 times (1M NaOH), the inflation was shifted to lower than 1 mL of AgNO<sub>3</sub>. Further increasing the concentration of NaOH by 1000 times, inflation was not observed. This result can be explained by comparative solubility product of AgCl and AgOH. The solubility product of AgOH (2x10<sup>-8</sup>) is slightly higher than that of AgCl (1x10<sup>-12</sup>), therefore the precipitation of AgCl was suppressed by the addition of excess of NaOH. Since Ag<sub>2</sub>S electrode does not



**Figure 2:** Titration of sodium chloride with silver nitrate in presence of sodium hydroxide

**Table I:** Comparison of results of thiamine hydrochloride in vitamin B1 tablet obtained from ISE method, IC method and CV method

Electrode No	ISE method (n=3)	Ion chromatographic (IC) method (n=3)	Cyclic Voltametric (CV) method (n=3)
1	63.7 % ± 0.03	64 % ± 0.01	64.25 % ± 0.01
2	63.8 % ± 0.02		
3	63.7 % ± 0.02		
4	63.7 % ± 0.03		

respond to OH<sup>-</sup> ion, the potential did not change. The visual observation of the titration showed no indication of any tint of AgCl precipitation.

#### Determination of thiamine hydrochloride in Pharmaceutical preparation (vitamin B<sub>1</sub> tablet)

*By estimating ionisable chloride in thiamine hydrochloride*

The amount of thiamine hydrochloride in a pharmaceutical preparation was determined by titrating it with silver nitrate (0.01 M) solution. From this titration, the amount of thiamine can be estimated indirectly by estimating ionisable chloride since per mole of thiamine releases 2 moles of chloride. The amount of thiamine hydrochloride estimated by ISE method was compared with that estimated by ion chromatography and cyclic voltammetry. The results are tabulated in table (I). In ISE method, all the measurements were repeated 3 times by using several electrodes to check the accuracy and reproducibility. The amount of thiamine estimated by ISE method was about 63.7 wt % which was almost similar to the one estimated by IC and CV methods.

#### By estimating replaceable protons in a chemically transformed thiamine hydrochloride in a highly alkaline medium

The method of determination of thiamine hydrochloride by titrating the free chloride with silver nitrate is quite sensitive and gives good results but it is not applicable for direct determination of thiamine in presence of chloride from other sources. In neutral and less alkaline solution, thiamine part of thiamine hydrochloride cannot be determined as chloride ion interferes. But at highly alkaline medium, chloride ions do not have any effect as shown in Fig (2). As described elsewhere [17] in highly alkaline medium, thiamine undergo chemical transformation and loses 2 protons through 2 distinct dissociation steps. The reaction occurs through intramolecular addition of the amino group of thiamine to the thiazolium ring with loss of 1 proton, accompanied by opening of the thiazole ring and loss of a second proton [23]. These protons are replaceable by Ag<sup>+</sup> ions. Then it was determined by silver sulphide electrode. Hence, under highly alkaline medium, silver sulphide electrode can be used as an indicator electrode for the determination of thiamine content in vitamin B<sub>1</sub> tablet.

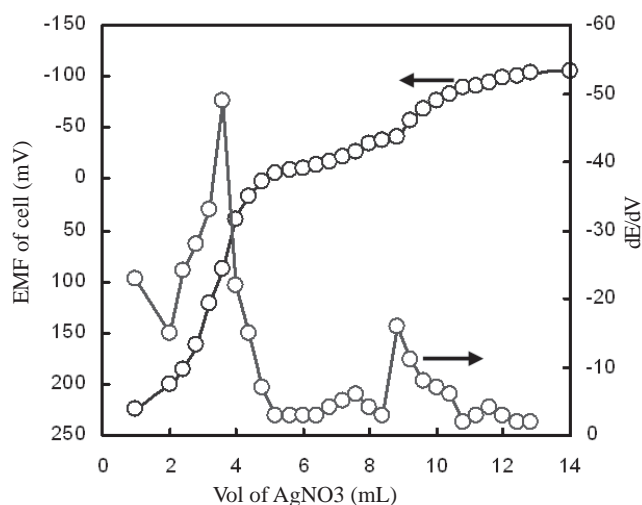
#### Determination of thiamine in vitamin B<sub>1</sub> tablet

In this method, 5 mL of sample solution was taken and made highly alkaline by adding required amount of NaOH. The amount of thiamine was estimated by the procedure described

above. Two potential breaks are obtained which is shown in Fig (3). These 2 potential breaks are not due to reaction of AgNO<sub>3</sub> with ionizable chlorides since the end point was not observed for the precipitation of AgCl in the excess of NaOH as showed in Fig (2). The number of moles of silver nitrate consumed per mole of thiamine at first and second end points are 0.76 and 1.60 respectively. However, the silver nitrate solution needs to be standardized using authentic thiamine hydrochloride. The 2 inflation points are similar to that obtained by pure authentic sample. This means that the amount of thiamine in pharmaceutical preparation can be determined by potentiometric titration with silver nitrate solution in highly alkaline medium using home made silver sulphide electrode. The concentration of NaOH should be 1000 times higher than the concentration of chloride ion in sample for successful application of this method.

**Figure 3:** Titration of real sample (vitamin B1 tablet) with silver nitrate in 0.5M sodium hydroxide.

#### CONCLUSION



The home made silver sulfide ion selective electrodes was used as an indicator electrode in argentometric titration. The method can be applied for the determination of thiamine hydrochloride in pharmaceutical preparation. If there is an absence of any other chloride sources in the pharmaceutical preparation, the determination of thiamine hydrochloride can be done simply by titrating with silver nitrate in neutral medium. However, in presence of chloride from other sources, thiamine can still be determined by titrating with silver nitrate solution in presence of high amount of sodium hydroxide (>1000 times) solution using silver- sulphide electrode.

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