

Determination of 2-Mercaptoethanol by Potentiometric Titration with Mercury (II) Chloride

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Abstract

A new, direct, rapid, simple, sensitive and accurate method for the determination of 2-Mercaptoethanol (Quick facts) or Mercury(II); The method is based on the using mercury (II) chloride solution as titrant (or reverse) in potentiometric titration depending on the first and second derivative differential procedure was used for all titrations; The method is suitable for the assay of 2-ME in micro amounts at a wide range of mass (15626.6-7.8133 μg) in 80 mL; The equivalence point is marked by a sharp peak in all instances and molar ratio of (Hg^{2+} : 2-ME) at inflection point (1:2). Accurate and precise results were obtained with an average error % of (0.1333-0.5667%) and a Relative Standard Deviation of (0.70499-0.1957%) respectively.

Keywords: 2-Mercaptoethanol (2-ME); Mercury (II); Potentiometric titration

Introduction

2-Mercaptoethanol; 2-ME is a clear, colorless liquid with disagreeable odor it is miscible in water and nearly all common organic solvents and Specific gravity 1.115, the structure of 2-ME shown in Figure 1. 2-ME is prepared by reaction of hydrogen sulfide gas with ethylene oxide, it is primarily used in clinical laboratories as a reducing agent, the clinical and medical use of 2-ME has increased considerably, whereby it is also used for living-cell transformation investigations, cell mediated cytotoxicity studies and studying the enzyme activity in cellular systems; In solution, especially at alkaline pH, 2-ME is readily oxidized in air to a disulfide; Because of this property; It is used as a chain transfer agent in the manufacture of PVC and as intermediate for the synthesis of PVC heat stabilizers, it is used as a building block to produce corp. protection products, pharmaceuticals, fibers, textiles, dyes, and dispersants, and used as a component of corrosion inhibitors and ore floatation agent.

In biochemistry, due to its strong reducing properties, it is studied in the activity of immune system or denatures the proteins, 2-ME denatures the proteins by reducing disulfide linkages leading to tautomerization and breaking up quaternary protein structure and has been studied as anti-cancer agent by acting as alkylation agent to damage the cancer cell DNA.

An excess of 2-ME (generally used at 0.01M) will maintain the protein thiol groups in their reduced state; Researchers have seen art factual bands in SDS-PAGE systems, appearing in the range of 54 to 68 kDa, particularly in 2-dimensional electrophoresis systems when sensitive staining techniques are used to detect proteins, such as gold or silver staining [1-4].

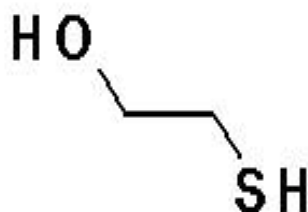


Figure 1: Chemical structure of 2-Mercaptoethanol.

Although these have appeared when 2-ME is used, they have been attributed to the action of 2-ME on some component in the system. These bands may be eliminated by removing the 2-ME from the protein sample during equilibration and replacing it by iodoacetamide, which reportedly improves recovery and detection of proteins [3,4].

Complexes of mercury species with 2-mercaptoethanol are widely used in reversed-phase separation because of its chemical structure, until now the reagent was not solely used for extraction of mercury species in any solid sample [5].

2-ME can be determined by means of two basic analytical procedures:-

- Identification of the -OH group.
- Identification of the -SH group, either by oxidation to disulfide or by reaction with metal ions and formation of mercaptides.

Determination of SH group is generally considered to be the most suitable procedure owing to its wide application ability and relatively better accuracy and simplicity. In the past, analysis of 2-ME has been done by redox titration (about 8 g), this procedure is lengthy (more than 20 min.); A GLC procedure was developed for the determination of 2-ME [6]. HPLC with fluorescence detection developed for the determination of 2-ME [7]. Determination of 2-ME in water samples after extraction by using homogeneous liquid-liquid micro-extraction and GC with FID [8]. 2-ME was titrated coulometrically with the generated iodine [9] and A carbon-paste electrode modified with iron (II) phthalocyanine (FePc) was used as a sensitive potentiometric sensor for determination of 2-ME in aqueous solutions [10]. HOE electrode has been further coated with Nafion or Tosflex ion-exchange membranes and used in the determination of concentration of 2-ME by direct potentiometry [11].

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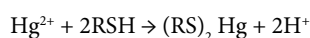
The complex tetraaminophthalocyanato-cobalt (II), electro-polymerized onto an electrode surface, serves as an excellent sensor for the quantitative estimation of 2-ME over a wide pH range [12].

Most of these methods for the quantitative estimation of 2-ME are time consuming, tedious, and expensive; require special devices, and not sensitive.

While 2-ME has been used to estimate some metals ions, such as spectrophotometric determination of Pd(II) with 2-ME, a yellow colored complex formed at ratio (1:2) in a (potassium hydrogen phthalate-hydrochloric acid) buffer pH 4 [13]. Indirect determination of Cu²⁺ using 2-ME as masking reagent [14], 2-ME used for the spectrophotometric determination of Se(II), the water soluble complex shows maximum absorption at (380 nm), and this was used as the basis for the spectrophotometric determination of Se [15]. Complexometric determination of Cd(II) using 2-ME as masking reagent [16]. Indirect complexometric determination of Bi(III) using 2-mercaptoethanol as masking agent [17] and Complexometric determination of indium(III) using 2-ME as masking agent [18].

The Potentiometric response using ordinary pyrolytic graphite electrodes (OPG) modified with cobalt phthalocyanine (Co-Pc) was used for determination of 2-ME thiols group in aqueous solutions at pH values between (11- 4) [19] these chemical methods for determinate of 2-ME (or used) are difficult, consume many chemicals, need calibration, extraction before determination and required special devices.

The mercaptane containing sample is titrated in neutral aqueous or acetone medium with mercury (II) ion as follow [20]:

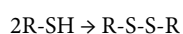


In this article, a new potentiometric titration method to determine 2-ME with mercury (II) chloride (or reverse) is described, the method presents good advantages such as short retention time and economy, and the method, being reasonably selective and accurate, it is simple and rapid as it does at room temperature.

Materials and Methods

Chemicals and reagents

Doubly distilled water was used throughout; 2-ME (SIGMA) purists was used (>99%); Its purity was determined by GC; The purity was found to be 99.9%; Standard solutions of (2×10^{-2} - 1×10^{-5} M) 2-ME were prepared daily in doubly, stored under an inert atmosphere of nitrogen to prevent aerial oxidation, under these conditions the composition of 2-ME was found to be unchanged 6 h after preparation, when a chemical analysis of 2-ME results show less than prepared to concentrate, because 2-ME is readily oxidized in air to a disulfide.



Mercuric chloride (BDH) 99.7% was dissolved to prepare solutions of (2×10^{-2} - 1×10^{-5} M). Sodium acetate (BDH) was dissolved to prepare solution of (0.2M).

Apparatus

Potentiometric titrations were carried out on Metrohm E536 automatic recording potentiograph with s Metrohm 655 multi-dosimat at a delivery rate of $2 \text{ mL} \cdot \text{min}^{-1}$. An 80 mL glass cell fitted with a Teflon lid containing five openings (two for the electrodes, one of the burette tip and the remaining two as inlet and outlet for the purified nitrogen); The indicating electrode was a bright platinum flag and the reference was a saturated calomel electrode; A silver/silver chloride-

platinum combined electrode was also used and gave the same results in all titrations; The later was preferred because of ease of handling and requires less space; It's preferred to clean the end of the indicating electrode after each titration by dipping into (0.1 M) nitric acid and washing with doubly distilled water.

Titration procedure

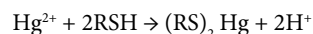
A 10 mL aliquot of the standard solution of 2-ME was transited by pipette into the titration vessel, and then 10 mL of sodium acetate (0.2 M) solution and doubly distilled water were added to bring the volume to capacity 80 mL.

The solution was stirred with a magnetic stirring bar; Purified nitrogen was bubbled through for about (2 min.) to de-aerate the solution and then directed over the solution surface to keep the titration under an atmosphere of nitrogen; The nitrogen was used to prevent any possible aerial oxidation of 2-ME to the disulphide; Titration with mercury (II) chloride solution was then started and continued until a sharp peak was obtained.

Or reverse transited 10 mL of Mercury (II) chloride solution into titration vessel and 10 mL of sodium acetate (0.2 M) then doubly distilled water were added to bring the volume to capacity 80 mL; Titration with 2-ME solution was then started and continued until a sharp peak was obtained; The first and second derivative differential procedure was used for all titrations and preferred to the normal S shaped titration curve because the end point was located more easily and more accurately.

Results and Discussion

The concentrations of 2-ME and mercury (II) chloride used in the range of (2×10^{-2} - 1×10^{-5} M); a mixture of 10 mL of 2-ME with 10 mL sodium acetate (0.2 M) and doubly distilled water were added to bring the volume to capacity 80 mL (15626.6 - $7.8133 \mu\text{g}$ of 2-ME in 80 mL), (pH=7.18) measured before titration, then titrated with an aqueous solution of mercury (II) chloride (2×10^{-2} - 1×10^{-5} M) (or reverse), a stable colorless complex was formed during the titration, the end point was demonstrated by a sharp and high peak at the equivalence point, occurred when the molar ratio of mercury (II) to 2-ME was 1: 2 as fallow [20]:



The (pH=5.22) measured after titration, the results of the titration of 2-ME with mercury (II) chloride are summarized in Table 1. Select time of titration ($10 \text{ minutes} = 2 \text{ mL} \cdot \text{min}^{-1}$) and the voltage at (750 mV), the range of detection limit and range of quantity limit of 2-ME concentrations determination are found at range (195.325 - $0.09766625 \mu\text{g} \cdot \text{mL}^{-1}$). The range of average error was found to be (0.1333-0.5667%). The range of recovery was found to be (99.4333-100.1333) and the range of relative standard deviation (0.70499 to 0.1957%) the present procedure proved to be selective, rapid and accurate; Results in a graph for the first derivative, as in Figure 2. Whereas when using the second derivative as in Figure 3.

The X-axis represents the volume of titrant on Figures 2 and 3 and the rate of addition of titrant ($2 \text{ mL} \cdot \text{min}^{-1}$) and the end point at 5 mL, therefore time consume 3 min. The potential rise at the equivalence point is quite pronounced in all the concentrations, however, be carried out successfully in presence of sufficient amount of sodium acetate. In all the concentrations, inflection occurs just after mole ratio (1:2) of mercury (II) chloride to 2-ME has been added (or reverse).

Comparison of present method with other methods in literature as in Table 2, shown, more sensitive range, less average error percentage,

Titrant	Amount of 2-ME μg		Average error %	Relative Standard deviation %	Recovery	Molar ratio at inflection point $\text{Hg}^{2+} : 2\text{-ME}$	Peak height cm
	Taken	Found'					
Hg^{2+}	15626.6	15647.435	0.1333	0.1957	100.1333	01:02.0	11-10
Hg^{2+}	781.33	776.90246	-0.5667	0.70499	99.4333	01:02.0	9-8
Hg^{2+}	78.133	78.237177	0.1333	0.53979	100.1333	01:02.0	7-5
Hg^{2+}	7.8133	7.81851	0.06667	0.471932	100.0667	01:02.0	5-3

*Six consecutive replicate solution of standard solution.

Table 1: Results of the titration of 2-ME with mercury (II) chloride.

Methods	Sensitive range	A.E % range	RSD % range	Recovery range	Time con.	Device and chemicals required	Ref.
Proposed method	15626.6 - 7.8133 μg	0.1333 to -0.5667	0.70499 to 0.1957	99.4333-100.1333	3 min	Ag/AgCl+Pt Com.E. Sod. Acetate	----
Coulometer	0.996 - 0.187 mg	0.5 to -2.0	$\pm 0.1 - \pm 0.9\%$	98.0-100.5	> 5min	biampereometric bipotentiometric GC20E potassium acetate in MeOH or EtOH potassium iodide or tetraethylammonium iodide	9
Potentiometer	5×10^{-3} - 1×10^{-6} M	0.13 to 0.08	$\pm 1.7 - 2.4\%$	99.87- 99.92	10min.	FePc- C paste E. phosphate buffer pH 7 (HOPC) electrode $\text{N},\text{N}',\text{N}'';\text{N}'''$ - tetramethyltetra-3,4- pyridinoporphyrazin cobalt(II) buffer phosphate	10
Potentiometer	2×10^{-3} - 5.7×10^{-5} M	----	$\pm 5.5\% - 2.5\%$,	----	30min.		11
Potentiometer	2×10^{-3} - 5.7×10^{-6} M	-----	$\pm 5.5\% - 2\%$	-----	20min.	electrodes CO \sim TAPC \sim and Co1TAF \sim c5.N	12

Table 2: Comparison of present method with others.

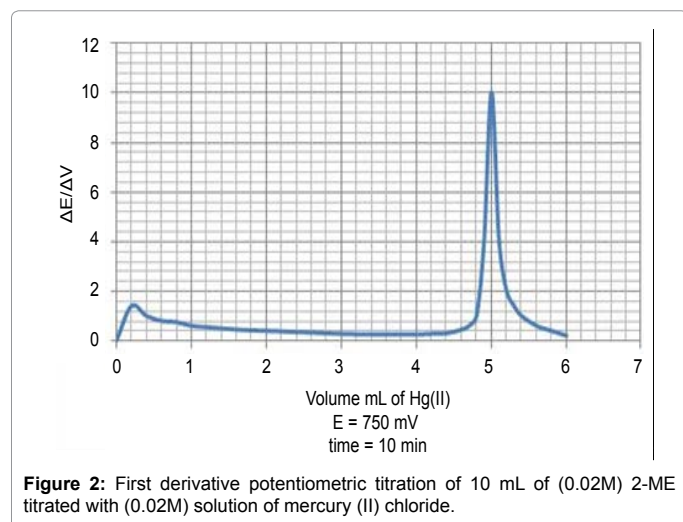


Figure 2: First derivative potentiometric titration of 10 mL of (0.02M) 2-ME titrated with (0.02M) solution of mercury (II) chloride.

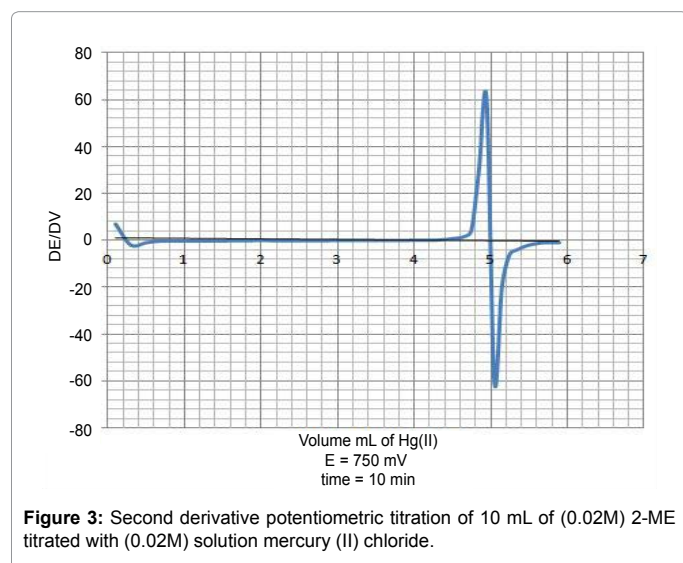


Figure 3: Second derivative potentiometric titration of 10 mL of (0.02M) 2-ME titrated with (0.02M) solution mercury (II) chloride.

less relative standard deviation, recovery range more accurate and less time consuming than other methods in literature, therefore this method direct, rapid, simple, sensitive and accurate method for the determination of 2-ME (Quick facts).

Conclusions

This method provides easy and accurate quantitation of 2-ME or mercury (II); the assay is performed at room temperature; maximum titration is attained within 3 minutes and is stable after prepare 2-ME solution for at least 6 hours, because 2-ME is readily oxidized in air to a disulfide.

The procedure for rapid estimation of 2-ME by potentiometric titration is given. 2-ME is titrated with a solution of mercury (II) chloride (Or reverse) in sodium acetate solution with use of platinum as an indicator electrode. A stable complex has been formed. A significant jump of the potential appears when the stoichiometric ratio of mercury (II) to 2-ME is 1:2.

The results show that this method is suitable for the determination of 2-ME in micro-quantities at a wide range of concentrations ($195.325 - 0.09766625 \mu\text{g.mL}^{-1}$).

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