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Short Communication

Potentiometric titration method for standardising aqueous sulfide solution

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Abstract

A simplified method is described for standardisation of aqueous sulfide solution using sulfide ion-selective electrode as the end-point detector and standard solutions of cadmium sulfate and lead nitrate as titrants. An alkaline antioxidant reagent has been used during tirtations to prevent loss of sulfide due to volatalisation and oxidation. The results obtained show that the method is highly precise and accurate when compared with the conventional iodimetric method for standardisation.

Key words: Potentiometric method, titration method, standardisation, sulfide solution.

1. Introduction

Determination of sulfide in water spectrophotometrically using ferric chloride and dimethyl-*p*-phenylene diamine producing methylene blue is a well-known method[1]. It, however, has a certain drawback concerning standardisation of aqueous sulfide solution. As the standard sulfide has to be prepared from $Na_2S \cdot 9H_2O$ containing a large amount of water of hydration, precise standards cannot be prepared by weighing the salt. Usually an approximate solution is first prepared and then it is standardised[2] by iodimetric titration which involves standardisation of iodine solution and sodium thiosulfate solution.

In the present paper, a simplified method is proposed for standardising aqueous sulfide solution using sulfide ion-selective electrode as the end-point detector and standard solutions of cadmium sulfate and lead nitrate as titrants. Use of an alkaline antioxidant reagent (AAR) containing sodium hydroxide and ascorbic acid has been made during titration to prevent loss of sulfide due to volatalisation and aerial oxidation. The results obtained show that the method is highly precise and accurate when compared with the conventional iodimetric method. Standard solution of silver nitrate was also tried as titrant but it gave no useful end-point because AAR could not be used during titration.

2. Experimental

2.1. *Outline of the method*

A sulfide ion-selective electrode[3] is an electro-chemical sensor having a solid-state element made from silver sulfide. The unique capacity of electrode to detect free sulfide ions in solution makes it a highly sensitive end-point detector in precipitation titrations. The titrant is so chosen that it forms highly insoluble precipitate with sulfide. The end-point is indicated by the greatest slope on the titration curve after all the sulfide in the solution gets precipitated. Since the titration is carried out in distilled water all interferences are eliminated. However, oxygen should be excluded from the titration apparatus as sulfides are susceptible to aerial oxidation. An alkaline antioxidant reagent has been used in the present method. The alkaline media helps in keeping the sulfide in S^{-2} form while the antioxidant inhibits the air oxidation of sulfide ions during titration. It also produces a stable electrode potential, eliminating complicated precautions such as purging of the sulfide solution with nitrogen and maintenance of nitrogen atmosphere during titration.

2.2. *Equipment*

Potential measurements were read from a digital mV meter (Model 901, Orion Research Inc., USA) provided with a relative millivolt mode. A sulfide ion-selective electrode (Model 94-16, Orion Research Inc., USA) was used as the end-point detector. A double junction electrode (Model 90-02, Orion Research Inc., USA) was used as the reference electrode. A magnetic stirrer having a speed control arrangement was used for stirring of solution. A microburette of 5 ml capacity having sub-divisions of 0·02 ml was used for adding the titrant.

2.3. *Reagents*

Deoxygenated distilled water was used in the method which was obtained by boiling distilled water for ten minutes and allowing it to cool before use.

An alkaline antioxidant reagent containing sodium hydroxide (5·0 M) and ascorbic acid (0·5 M) was prepared by dissolving 50 g of NaOH (A.R. grade) and 20 g of ascorbic acid (A.R. grade) in 250 ml of deoxyganated distilled water. Ascorbic acid was included as antioxidant[4]. Fresh AAR was found to have pale yellow-brown colour. This solution had a shelf-life of about [illegible] week depending upon its exposure to air. When AAR turned dark brown, due to oxidation, it was rejected. The reagent was stored in a tightly stoppered polyethylene bottle. Its life was found extended by storing it in refrigerator.

A stock solution of sulfide was prepared by weighing out 3·75 g of driest looking crystals of sodium sulfide (nonahydrate) $Na_2S \cdot 9H_2O$ in 500 ml of deoxygenated distilled water. One ml of this solution corresponds to approximately one mg of sulfide. This solution was stored in a tightly stoppered polyethylene bottle. Dilute solution (1 ml = 0·1 mg S^{-2}) was prepared by dilution.

Standard solutions (250 ml each) of the titrants such as cadmium sulfate (0·0312 N), lead nitrate (0·0312 N) and silver nitrate (0·0624 N) were prepared by dissolving 2·007 g of $3\ CdSO_4 \cdot 8H_2O$; 2·5834 g of $Pb\ (NO_3)_2$ and 2·6499 g of $AgNO_3$. All of them were of A.R. grade. The normality of the titrants was so chosen that one ml of the solution corresponds to one mg of sulfide.

2.4. *Titration procedure*

The electrodes connected previously to a mV meter were immersed into the sulfide solution containing magnetic stirrer bar and the stirrer was started. The titrant was added from a microburette in increments of 0·2–0·4 ml in the beginning of the titration. At each interval when a steady potential was reached (usually 30 seconds were required) the potential reading (mV) was recorded. In the vicinity of the end-point (indicated by the rapidly changing potential) the titrant was added in increments of 0·02 ml. A longer response time (approximately 2–3 minutes) was observed in the region of end-point. The titration was continued beyond the end-point by adding titrant further in increments of 0·2–0·4 ml until an excess of 30–40% of the titrant was added. The potential readings were plotted on the *y*-axis against the titrant volume on the *x*-axis.

3. Results and discussion

A large potential change was observed during titrations near the end-point which makes it possible to take readings with any pH or mV meter without using an expanded scale. It is also not necessary to plot the entire potential/volume readings in order to determine the end-point. It is sufficient to plot the titration curve in the region of rapidly changing potential to find the end-point.

Alkaline antioxidant reagent could not be used with silver nitrate as titrant because it caused reduction of silver ions to silver metal. But while using cadmium sulfate and lead nitrate as titrants it was found that lead and cadmium ions were not affected by AAR. The titration curves were found to be symmetrical. A typical titration curve obtained with cadmium sulfate and lead nitrate as titrant is shown in fig. 1.

The values of sulfide concentration obtained by this method have been compared with those obtained by the conventional iodimetric method of standardisation. Low

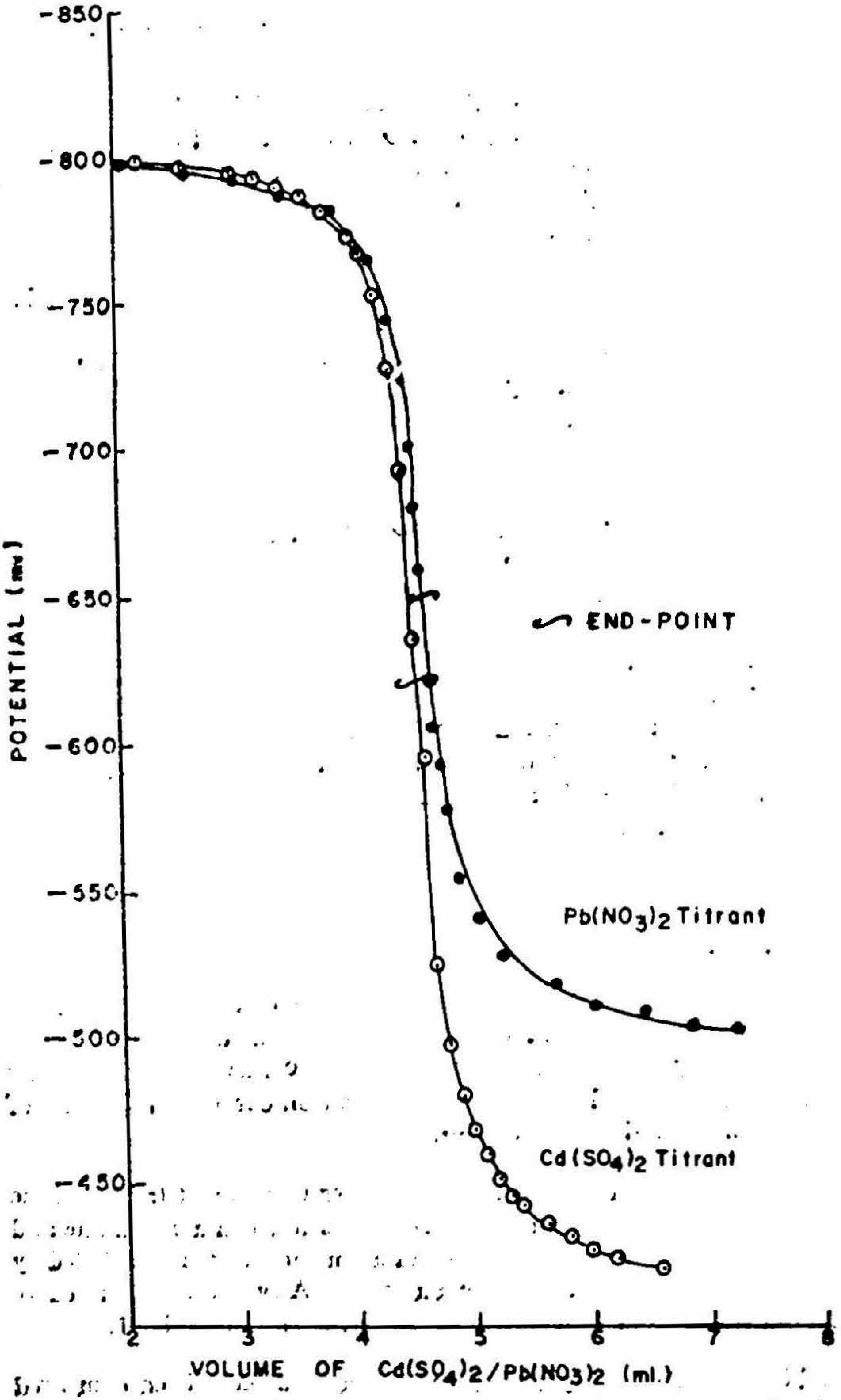

FIG. 1. A typical titration curve obtained with cadmium sulfate and lead nitrate as titrant.

values of sulfide content were observed in the absence of alkaline antioxidant reagent. The relative standard deviation and the relative mean error from eight replicate titrations show that the potentiometric method for standardisation of aqueous sulfide solution using cadmium sulfate (Table I) and lead nitrate (Table II) as titrant is highly precise and accurate when compared with the conventional iodimetric method.

Table I

Precision and accuracy data (*Cadmium sulfate titrant*)

Sulfide level (mg)	Iodimetric method sulfide found (mg)	Sulfide found (mg) — Replicate analysis	Mean	Mean error (mg)	Relative mean error %	Standard deviation (mg)	Relative standard deviation %
2·5	2·32	2·30, 2·26, 2·28, 2·30, 2·28, 2·26 2·28, 2·30	2·28	0·04	1·7	0·02	0·7
5·0	4·60	4·60, 4·54, 4·50, 4·48, 4·56, 4·52, 4·58, 4·56	4·54	0·06	1·3	0·04	0·9
10·0	9·24	9·08, 9·10, 9·14, 9·12, 9·20, 9·18, 9·10, 9·18	9·14	0·10	1·1	0·05	0·6

Table II

Precision and accuracy data (*Lead nitrate titrant*)

Sulfide level (mg)	Iodimetric method sulfide found (mg)	Sulfide found (mg)		Mean error (mg)	Relative mean error %	Standard deviation (mg)	Relative standard deviation %
		Replicate Analysis	Mean				
2·5	2·32	2·30, 2·32, 2·32, 2·28, 2·28, 2·28, 2·30, 2·30	2·30	0·02	0·9	0·02	0·7
5·0	4·60	4·54, 4·52, 4·52, 4·54, 4·48, 4·48, 4·56, 4·50	4·52	0·08	1·7	0·03	0·6
10·0	9·24	9·02, 9·18, 9·16, 9·04, 9·06, 9·14, 9·08, 9·14	9·14	0·14	1·5	0·06	0·7

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