

POTENTIOMETRIC DETERMINATION OF SULPHITE IN THE PRESENCE OF THIOSULPHATE, SULPHIDE, SULPHATE AND Fe (II)

M. Sarwar, A. Rashid, M. Azam* and M. Hafeez*

PCSIR Laboratories, Lahore-16

(Received June 18, 1984; revised November 6, 1986)

In this procedure potentiometric determination of sodium sulphite is described. N-Bromosuccinimide has been used as titrant. 10 to 50 mg samples of sodium sulphite were analysed with maximum error of 1.0 % when 10.0 mg sample was taken. Nitrogen gas was passed in the reaction vessel during titration. Interferences due to thiosulphate, sulphide, sulphate and Fe^{2+} have also been studied and removed.

Key words: Potentiometry, Sulphite, Thiosulphate.

INTRODUCTION

Sulphites are notorious compounds in the sense that they present a serious problem in their determination because they get easily oxidized by the atmospheric oxygen. There are a number of methods available for their determination. The widely used method for the determination of sulphites is by iodometry [1-6]. In this method sample is added to an excess of iodine solution and after the reaction has completed the excess is back titrated with standard sodium thiosulphate solution. In this method both iodine and sodium thiosulphate need careful and repeated standardizations, thus making the method a little time consuming.

Numerous other iodometric determinations of sulphites and thiosulphates in the presence of each other are available in literature [7-23]. In these methods an oxidant is added to the sample, after sulphite has been complexed with formaldehyde. Formaldehyde when present in excess presents serious problem in these determinations because it can also get easily oxidized by the iodine or other oxidants.

Among the instrumental methods for the determination of sulphites one is by adding iodine to the sample solution and then measuring the excess of iodine photometrically [24]. In a similar method an excess of potassium dichromate solution is added and after the reaction the excess of dichromate is measured photometrically [25].

Another photometric method is available in which sulphite ions and other sulphur compounds are reduced to H_2S with aluminium metal in acid medium. The resultant H_2S is absorbed in lead citrate solution and then the lead sulphide suspension is measured photometrically [26].

Methylene Blue complex of iodine reacts with sulphites and liberates Methylene Blue, which can be determined photometrically [27]. Fuchsin and p-Rosaniline, in the presence of formaldehyde complex with sulphites to give a coloured compound which forms the basis of its colorimetric determination [28-30]. When Methyl-Green or Malachite-Green react with sulphites their colour is bleached. This property has been utilized for the colorimetric determination of sulphites [31-32]. Similarly sodium nitroprusside reacts with sulphites in the presence of zinc to give a red complex which can be measured colorimetrically [33-34]. All these methods are not specific for sulphites because other interfering ions like sulphide, thiosulphate etc. have not been investigated.

One of the most sensitive methods for the determination of sulphites is polarographically [35-38] but the disadvantage of this method is that other compounds like sulphide and thiosulphate interfere in the determination.

Ion chromatography [39-43] has been used for monitoring the sulphite contents in industrial process water, pulp-ling liquors and photographic processing solutions but a number of ions interfere.

Mn (IV) [44] has also been used for titrimetric determination of sulphite and the excess of Mn (VI) added is back titrated with Fe (II) which is itself not stable and a number of standardizations add to more errors.

Potentiometric [45] determination of sulphite has also been tried using lead sensitive ion-selective-electrode in a standard solution of $\text{Pb}(\text{ClO}_4)_2$ in 50 % methyl alcohol. The potential difference before and after addition of sample is recorded, which is compared with standard and the % error reported is high.

In the present investigation an attempt has been made to determine sulphite potentiometrically using N-Bromo-

*Government College of Science, Lahore.

succinimide as a titrant. An effort has been also made to titrate sulphite in presence of sulphide, thiosulphate and ferrous. The standard solution of N-Bromosuccinimide is fairly stable when refrigerated and protected from light [46]. This reagent has oxidizing potential of 1.1V in neutral solution [47] and is also easy to handle as compared to iodine, hypobromite or hypochlorite solutions, therefore its usefulness has been extended for the determination of sulphites. The method is rapid, precise and accurate.

EXPERIMENTAL

Apparatus. (a) All e.m.f. measurements were made with Radelkis universal pH meter, type: OP 204/I. Platinum strip indicating electrode was used against saturated calomel reference electrode. (b) Burette. 10 ml graduated at 0.02 ml intervals. (c) Pipette. 10 ml graduated at 0.10 ml intervals. (d) The reaction vessel was a 250 ml lipless beaker fitted with a rubber cover having four holes for electrodes, burette and nitrogen gas.

Reagents. (a) N-Bromosuccinimide: A 0.1N solution of N-Bromosuccinimide was prepared by dissolving 890 mg of recrystallized stuff in nitrogen flushed distilled water and making the volume upto 100 ml. (b) Sodium sulphite: It was a BDH analar product and was standardized iodometrically [5]. Similarly Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2S and FeSO_4 , were also of analytical grade and the dilutions were made to required molarities as in (a).

Procedure

The potentiometer was standardized with the known system of $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$. 10 mg Na_2SO_3 (solid) was added to the reaction vessel followed by the addition of 80 ml of nitrogen passed distilled water. Then the electrodes were dipped into it. Nitrogen gas was passed continuously for the exclusion of atmospheric oxygen. After magnetic stirring the e.m.f of the cell containing the sulphite solution was taken. Then this solution was titrated with 0.1N N-bromosuccinimide adding by small installments from the microburette and e.m.f. was noted. The installments were further reduced near the equivalence point. The installments from the microburette and e.m.f. was noted. The $\frac{\Delta E}{\Delta V}$ volume of the titrant used was located from the graph when $\frac{\Delta E}{\Delta V}$ was plotted against V.

Calculations

$$\text{Amount of Sodium Sulphite (mg)} = N \times V \times E$$

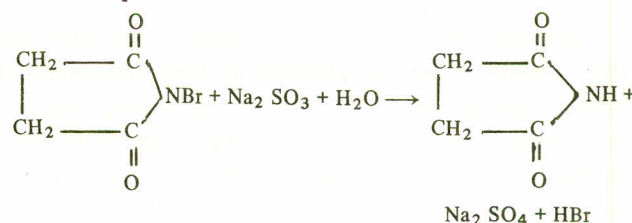
N = Normality of N-Bromosuccinimide.

V = Volume of N-Bromosuccinimide used in the titer.

E = Equivalent weight of sodium sulphite.

RESULTS AND DISCUSSION

N-Bromosuccinimide has been used frequently for the determination of various substances [48-57]. In these determinations the oxidizing property of Br^+ or its addition property at the double bond has been utilized. In many determinations Bordeaux red has been used as indicator where its blank has to be subtracted from the titer. In this investigation an attempt has been made to determine sulphite potentiometrically by using NBS as titrant because it has oxidizing potential of 1.1V in neutral medium [40]. In this case no blank is required and the results obtained are more precise and accurate. The reaction between sulphite and NBS is shown below:



The stoichiometry of the reaction is proved by the accurate results shown in Table 1. The maximum error was 1.0 % when a 10 mg sample was analysed.

The typical titration curve of 10.0 mg sample of Na_2SO_3 against 0.01N NBS is shown in Fig. 1.

Effect of thiosulphate on the determination of sulphite.

The tolerance limit for thiosulphate in the determination of sulphite is 0.2 mg in a 10 mg sample of sulphite. However, when greater amounts were present, it did interfere in the determination of sulphite. But this interference was removed by the addition of lead nitrate. The results are shown in Table 2.

Table 1. Potentiometric determination of sodium sulphite

Amount taken (mg)	Amount found (mg)	% error
10.0	9.9	- 1.0
12.0	11.9	- 0.8
15.0	14.9	- 0.6
20.0	19.9	- 0.5
30.0	29.9	- 0.3
40.0	39.9	- 0.2
50.0	49.8	- 0.2

Effect of sulphide on the determination of sulphite.

Sulphite was also determined in the presence of sodium sulphide. It has been found that when 0.1 mg sodium sulphide was present in 10 mg sample of sulphite it did not have any effect on the determination. But when more than this limit was present, it did interfere. The results are shown in Table 3. This interference can be removed by the addition of lead nitrate solution to sample containing sulphide.

Effect of sulphate on the determination of sulphite.

Sulphate does not interfere in the determination of sulphite even if present in equal amounts.

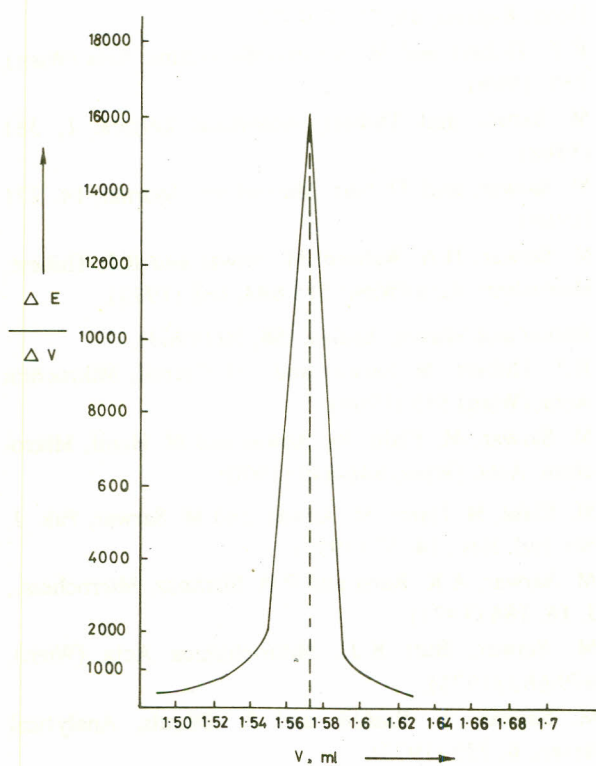


Fig. 1. A typical potentiometric curve of $\frac{\Delta E}{\Delta V}$ vs. V .

Table 2. Determination of sulphite in presence of thiosulphate

Amount taken (mg)	Thiosulphate		% error
	added (mg)	Amount found (mg)	
10.0	0.1	9.9	- 1.0
10.0	0.2	9.9	- 1.0
10.0	0.3	10.2	+ 2.0
10.0	0.4	10.3	+ 3.0
10.0	0.5	10.4	+ 4.0

Table 3

Amount taken (mg)	Thiosulphate		% error
	added (mg)	Amount found (mg)	
10.0	0.1	9.9	- 1.0
10.0	0.2	10.1	+ 1.0
10.0	0.3	10.2	+ 2.0
10.0	0.4	10.3	+ 3.0
10.0	0.5	10.5	+ 5.0

Effect of Fe²⁺ on the determination of sulphite. Iron (II) also interferes in the determination of sulphite. This interference was removed by complexing Fe (II) with 2-2 dipyrindyl in test sample.

The method described is simple, convenient and less time consuming than the existing methods. Since only one reagent, N-Bromosuccinimide is required.

REFERENCES

- H. Rose and R. Finkener, *Handb. Anal. Chem.*, 6th Ed. Leipzig 1871.
- F. Reschig, *Z. Angew. Chem.*, **17**, 477 (1904).
- O. Ruff and W. Jaroch, *Ber.*, **38**, 409 (1905).
- H.I. Waterman, *Chem. Weekblad.*, **17**, 196 (1920).
- I.M. Kolthoff, *Z. Anal. Chem.*, **60**, 448 (1921).
- H.M. Mason and G. Walsh, *Analyst*, **53**, 142 (1928).
- A. Kurtenacker, *Z. Anal. Chem.*, **64**, 56 (1924).
- R. Wollak, *Z. Anal. Chem.*, **77**, 401 (1929).
- A. Kurtenacker and R. Wollak, *Z. Anorg. Allgem. Chem.*, **161**, 201 (1927).
- A. Brau, *Ann. Chim. Anal. Chim., Appl.*, **19**, 38 (1937).
- G. Charlot, *Ann. Chim. (Paris)*, **27**, 153 (1945).
- A. Hemmler, *Ann. Chim. Appliquee*, **28**, 419 (1938).
- I.M. Kolthoff, *Pharm. weekblad*, **56**, 572 (1919).
- A. Kurtenacker and K. Bittner, *Z. Anorg. Allgem. Chem.* **141**, 297 (1924).
- A. Kurtenacker and A. Fritsch, *Z. Anorg. Allgem. Chem.*, **117**, 262 (1921).
- C. Maye and J. Peyfuss, *Z. Anorg. Chem.*, **127**, 123 (1923).
- G. Lunge and J.H. Smith, *J. Soc. Chem. Ind.*, **3**, 460 (1933).
- G. Lunge and D. Segaller, *J. Soc. Chem. Ind.*, **19**, 221 (1900).
- K.G.A. Pankhurst, *Chem. Ind. London*, **74**, (1942).
- E. Schulek and L. Maros, *Magy. Kem. Folyoirat*, **63**, 61, (1957).

21. A.R. Vaseduve, *Sci. Ind.*, **22**, 342 (1953).
22. V.K. Duboveya and A.D. Miller, *Nekotorye vopt. knim. Tekhnol. i. Fiz. Khim. Analiza Neorgan. sistem. Akad. Nauk. Uz. SSR, otd. Khim. Nauk.*, 184 (1963).
23. D.N. Fogg and N.T. Wilkinson, *J. Appl. Chem.*, **2**, 357 (1952).
24. T. Ozava, *Nippon Kagaku Zasshi*, **87**, 573 (1966).
25. S. Susman and J.L. Portnoy, *Anal. Chem.* **24**, 1652 (1952).
26. F. Cuta, M. Hejtmanek and Z. Kurcera, *Z. Anal. Chem.*, **154**, 150 (1957).
27. T. Kato, *Nippon Kagaku Zesshi*, **80**, 1254 (1959).
28. J.M. Koreman, F. S-Frum and A.A. Rusakich, *Zadovak. Lab.*, **16**, 3 (1950).
29. Y. Arikana, T. Ozawa and I. Iwesaki, *Bull. Chem. Soc. Japan*, **41**, 1454 (1968).
30. A. Staigman, *Anal. Chem.*, **22**, 492 (1950).
31. S. Honda, *Osaka Kogyo Gijutsu Shikensho Kiho*, **17**, 84 (1966).
32. Idem, *Osaka Kogyo Gijutsu Shikensho Kiho* **17**, 89 (1966).
33. A.G. Fogg, W. Moser and R.A. Chalmers, *Annl. Chim. Acta.*, **36**, 248 (1966).
34. P. Bourbon and R.A.M. Malbose, French patent, 542, 1, 703 (18 Oct. 1968).
35. B. Gosman, *Collection Czech, Chem. Commun*, **2**, 185 (1930).
36. I.M. Kolthoff and G.S. Miller, *J. Am. Chem. Soc.*, **63**, 2818 (1941).
37. N. Kh. Tumanova and Yu. K. Delimerskii, *Ukr. Khim. Zh.*, **30**, 796 (1964).
38. G. Raspi and G. Ciantelli, *Chim. Ind. (Milan)* **47**, 1325 (1965).
39. M. Sarwar and R.J. Thibert, *Microchim. Acta. (Wien)*, 259 (1969).
40. G.O. Frankling *Pulping Conf. (Prof.)* 255 (1981).
41. J.A. Raway *Anal. Environ. Pollut.*, **2**, 245 (1979).
42. M. Matsomoto, *Taiki Osen Gakkaishi Japan* **19**, 247 (1984).
43. M.J. Mclormick and L.M. Dixon, *J. Chromatogr.*, **322**, 478 (1985).
44. J. Muralikrishem and K. Subrahmoryam, *J. Inst. Chem. (India)*, **56**, 245 (1984).
45. M. Volentova, J. Vrbsby and H. Tramondlova, *Sb. Vgs Sk. Chem. Technol-Praze Anal. Chem.*, **H 19**, 97 (1984).
46. M. Sarwar, I. Haque, B.A. Khokher and G.M. Zia, *Denki Kagaku*, **45**, 515 (1977).
47. R.T. Thibert and M. Sarwar *Microchim. Acta (Wien)*, 259 (1969).
48. M. Sarwar and Thibert. *Analytical Letters*, **1**, 381 (1968).
49. M. Sarwar, and Thibert. *Microchem. Journal*, **14**, 271 (1969).
50. M. Sarwar, H.A. Waheed, M. Anwar and R.J. Thibert, *Microchim. Acta (Wien)* 515 **683**, 688 (1973).
51. Barkat and Shaker, *Analyst*, **88**, 59 (1963).
52. R.J. Thibert. M. Sarwar and J.B. Carroll, *Mikrochim Acta, (Wien)* 555 (1969).
53. M. Sarwar, M. Elahi, M. Anwar and M. Hanif, *Mikrochim. Acta, (Wien)* 846-849 (1970).
54. M. Elahi, M. Hanif, M. Anwar, and M. Sarwar, *Pak. J. Sci. Ind. Res.*, **14**, 57 (1971).
55. M. Sarwar, A.K. Rana and P.H. Shahnaz, *Microchem.*, **J. 16**, 184 (1971).
56. M. Sarwar, Butt K.J., *Mikrochimica Acta (Wien)*, 679-682 (1973).
57. M. Sarwar, A. Rashid, and F. Bilquis, *Analytical letters*, **6**, 755 (1973).