

## THE DETERMINATION OF SULPHIDE AND SULPHITE WITH COBALT(III) ACETATE AS TITRIMETRIC REAGENT

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**Abstract.** A new method for the accurate and precise determination of sulphide and sulphite even in  $\mu\text{g}$  amounts, based on their direct oxidation by cobalt(III) has been developed. Since cobalt(III) acetate in glacial acetic acid, is stable for at least a month hence there is no need of its repeated standardization. Sulphide within the limits of 8.50 mg–150.80  $\mu\text{g}$  and sulphite from 7.28 mg to 123.98  $\mu\text{g}$  can be safely determined showing an average standard deviation of 0.34 and 0.19% respectively.

We have earlier reported<sup>1-5</sup> the preparation of a stable solution of cobalt(III) acetate in glacial acetic acid, its shelf-life, and the use of its strong oxidising properties for the estimation of various inorganic and organic substances potentiometrically. Other authors have also utilised this titrant for the quantitative determination of  $\text{Fe}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Sn}^{+2}$ ,  $\text{I}^-$ , some derivatives of hydrazine, ascorbic acid, cysteine,<sup>6-8</sup> gentisic acid and its derivatives and hydroxynaphthalenes.<sup>9,10</sup> During these investigations the titrant has proved its worth for its analytical uses. The high stability of its solution in glacial acetic acid has lent added initiative for further investigations regarding its usefulness as a potential titrant.

In view of the above very encouraging situation, we, in order to extend the potential uses of this titrant, have further investigated the suitability of this oxidimetric titrimetric reagent for the estimation of sulphide and sulphite.

### Experimental

#### Reagents

**Cobalt(III) Acetate.** An appropriate solution, was prepared<sup>2</sup> electrolytically and it was standardised with iron(II) in 2N HCl using a potentiometric end-point method.<sup>6</sup>

**Sodium Sulphide.** The required solution was prepared from analytical grade reagent ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) and standardised against *N*-bromosuccinimide.<sup>11</sup>

**Sodium Sulphite.** A solution of the required strength was prepared from  $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$  (analytical grade) and its factor was iodimetrically checked.

All other reagents used were either of analytical grade or of equivalent purity.

**Apparatus.** Potential measurements were made with an electronic potentiometer (Pye, Cambridge), with a platinum-indicator electrode and a saturated calomel-reference electrode. The electrodes were well washed with distilled water after each titration. The platinum electrode, after each titration, was rubbed between the folds of filter-paper to remove any substance adhering to its surface.

**Procedure.** An aliquot of the test solution (0.5–25

ml for sulphide and 1.0–40.0 for ml sulphite) was taken in a 250-ml Pyrex glass beaker and distilled water was added to bring the volume of the reactants to 125 ml and 80 ml for sulphide and sulphite respectively. The titration was performed by adding standardised cobalt(III) acetate solution from a 5-ml burette graduated at 0.02 ml intervals. The titrant near the equivalence point, was added in 0.02 ml increments. The titration was followed potentiometrically.

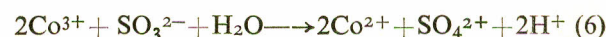
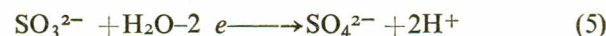
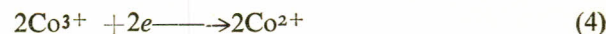
#### Calculations

$$\text{Amount of sulphide or sulphite (mg)} = N \times V \times E$$

Where *N*, normality of cobalt(III) acetate; *V*, volume (ml) of cobalt(III) acetate used for titer and *E*, milliequivalent weight of the sulphide or sulphite.

### Results and Discussion

The data shown in Table 1–4 for each reading is the mean of 7 titrations. The determination of sulphide and sulphite is accomplished by the direct oxidation of sulphide according to the following equations:



**Oxidation of Sulphide.** The electronic changes represented in equations 1–3 have been taken into consideration for various calculations of normalities or equivalent weights of the respective substances. It is obvious from Table 1 that cobalt(III) acetate prepared in glacial acetic acid, can determine sulphide even in mg to  $\mu\text{g}$  amounts with a maximum relative standard deviation of 0.87%. The potential jump at equivalence point is quite high due to which the volume consumption of the titrant could be read with

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TABLE 1. DETERMINATION OF SULPHIDE AND SULPHITE.

Taken	Found	Standard deviation (%)
<i>Sulphide</i>		
150.80 $\mu\text{g}$	150.64 $\mu\text{g}$	0.10
288.00 "	288.07 "	0.26
455.00 "	454.83 "	0.26
576.00 "	574.02 "	0.01
1.73 mg	1.72 mg	0.41
2.88 "	2.87 "	0.31
5.76 "	5.75 "	0.46
8.50 "	8.47 "	0.87
<i>Sulphite</i>		
123.98 $\mu\text{g}$	123.59 $\mu\text{g}$	0.01
371.95 "	370.92 "	0.01
413.28 "	412.29 "	0.00
588.92 "	587.38 "	0.00
785.23 "	784.17 "	0.01
948.45 "	945.75 "	0.00
1.90 mg	1.89 mg	0.57
2.48 "	2.50 "	0.32
3.72 "	3.69 "	0.24
5.46 "	5.42 "	0.36
6.20 "	6.15 "	0.65
7.28 "	7.45 "	0.13

reasonable accuracy. The potential stabilisation after each addition of the titrant is quick. The inflection potential was at 650 mV and  $\Delta\text{mV}/\Delta\text{ml}$  for 0.02 ml of 0.1N Co(III) acetate was 20.

*Oxidation of Sulphite.* Similarly equations (4-6) represent the course of reaction for sulphite oxidation with  $\text{Co}^{3+}$ . These electronic changes were taken into consideration for the calculation of equivalent weights of the respective substances. It is clear from Table 1

that sulphite could be successfully determined from 7.28 mg down to 123.98  $\mu\text{g}$  with maximum standard deviation of 0.65 and 0.01% respectively. The potential stabilisation before equivalence point is quick as compared to that after it. A good potential jump is observed at inflection thereby easy and accurate evaluation of the titrant being used for a complete titration. Inflection potential was at about 600 mV and  $\Delta\text{mV}/\Delta\text{ml}$  for 0.02 ml of 0.1N Co(III) acetate was 25.

The methods described here for the determination of sulphide and sulphite are quite rapid, precise and accurate. Further work on the estimation of sulphur in organic compounds with cobalt(III) acetate, is in progress.

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