A MODIFIED METHOD FOR THE DETERMINATION OF ARSENITE WITH COBALT(III) ACETATE

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Abstract. A modified, quick and precise method for the quantitative determination of As(III) with cobalt(III) acetate in 1N HCl as medium has been devised. The slow rate of reaction between cobalt (III) and As(III) has been accelerated by the addition of catalysts. Effect of interferences on the reaction has also been studied.

In our previous communications [1–3] we have successfully utilized the strong oxidizing power of cobalt (III) acetate for the estimation of many organic and inorganic substances. Formal redox potential values of Co^{3+}/Co^{2+} system in various acid media, with regard to using it as a redox titrant, have also been reported in our recent communication.[4]

Pszonicka and Minczewaski[5] while publishing their results on the analytical uses of cobalt(III) acetate gave the determinations of As(III) in 8N HCl, which is a very high concentration of the acid. This study, besides the aforesaid, is lacking in various other aspects such as no effect of interferences was studied. At the same time, it has also been reported in that communication that one must wait from 3–5 min after each addition of the titrant. This means a very slow reaction. The well-known method for As(III) estimation by iodine titration[6] suffers from the set back of repeated standardization of iodine soultion for a large number of runs. This makes iodine standardization method less accurate and time consuming.

In view of the situation it was felt desirable to do exhaustive studies on the quantitative determination of As(III), i.e. looking for any possibility of using some other acid as medium or at least low concentrations of HCl (because as high as 8N HCl is not only uneconomical but also not safe to handle) and then to try various catalysts to increase the rate of reaction to the extent where the reaction could be used practically. It was also considered necessary to study the effect of other ions on the quantitative determination of As (III). In the present work an attempt has there fore been made to estimate As(III) using cobalt (III)acetate as a volumetric reagent. Cobalt(III) acetate prepared in glacial acetic acid keeps its factor fairly constant over a number of days.[7] This method eliminates the drawback of repeated standardization of the titrant even for a number of runs.

Experimental

Reagents. As(III) solution was prepared in the usual way by dissolving 150 mg dried arsenous oxide (A.R. Grade) in 250 ml distilled water and standardizing iodometrically.[6] Solutions of low concentrations were obtained by exact dilutions of the above.

Cobalt(III) acetate solution in glacial acetic acid was prepared by the anodic oxidation method of Sharp and White[8] as modified by Hanif.[7] The factor of the prepared solutions was checked against standard ferrous sulphate in 2N HCl potentiometrically.[5] All other reagents used were of analytical grade.

Apparatus. Potential measurements were made with a pH meter (manufactured by W.G. Pye & Co. Ltd., Cambridge, England), using platinum foil as indicator electrode and saturated calomel as reference electrode.

Procedure. An accurately measured volume (1 ml) of the test solution was diluted with water and HCl, to approximately 80 ml in a 250-ml beaker. The solution thus obtained was 1N with respect to HCl. About 1.5 ml 0.1M silver nitrate was added as catalyst to the contents of the beaker. Titration was carried out by running cobalt(III) acetate solution from a 5-ml microburette graduated at 0.02 ml intervals. Potentiometric end-point method was used during these titrations.

Calculations. Amount of As(III) in mg $= N \times V \times E$ where N=normality of cobalt(III) acetate solutions; V=volume (ml) of cobalt(III) acetate used for titre; E=equivalent weight of arsenous oxide.

Interferences. To see the effect of interferences, 1–3 ml of 0.1N solution of each of the ions under test was added to the contents of the reaction vessel and titration was then run.

The following ions were tested for their possible interference with As(III) determination:

NO₂′, S″, S₂O₃″, Sn(II), Sb(III), Bi(III).

Catalysts. Sodium acetate, potassium acetate and silver nitrate solutions (0.1M, 1–3 ml, for one run) were tried as catalysts. The method of rapid addition besides heating reaction contents was also tried to see whether this could significantly increase the rate of reaction.

Results and Discussion

As(III), as evident from Tables 1 and 2, can be quantitatively oxidized to As(V) in as low concentration as 1N hydrochloric acid in about 80 ml total volume and with reasonable rate of reaction using silver nitrate as catalyst. The reaction can be represented as follows:

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Table 1. Determination of As(III) in 1n HCl using Silver Nitrate Catalyst.

Arsenic taken (mg)	Arsenic found* (mg)	Relative standard deviation (%)
1.80	1.80	0.56
3.00	3.00	0.33
4.80	4.79	0.03
6.00	5.99	0.33
9.00	8.98	0.11
12.00	11.98	0.08

*Each value is the average of seven readings

Table 2. Determination of As(III) in 1n HCl using Silver Nitrate as Catalyst.

Arsenic taken (μg)	Arsenic found* (μg)	Relative standard deviation (%)
600.00	598.94	1.28
700.00	701.85	0.32
800.00	802.77	0.36
850.00	851.21	0.30
950.00	950.41	0.22

*Each value is the average of seven readings

$$2Co^{3+} + As^{3+} \longrightarrow 2Co^{2+} + As^{5+} \qquad (1)$$
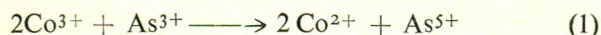
These electronic changes were taken into consideration for the determination equivalent of weights of the substances.

In order to increase the rate of reaction between Co(III) and As(III), sodium acetate, potassium acetate and silver nitrate were tried as catalysts. 0.1M silver nitrate solutions turned out to be the best catalyst. One titration was completed in 8–15 min. The potential stabilization was reasonably quick after each addition of the titrant. 1.5 ml of this solution was the optimum volume to be added. No appreciable change in reaction rate was noted even when the contents of the reaction vessel were heated to 40–50°C. Rapid addition of the titrant resulted in cutting down titration time but not significantly.

Addition of ions like NO_2', S'', S_2O_3'', Sn(II), Sb(III) and Bi(III) yielded results with positive error of As(III) estimation. This is due to the partial oxidation of these ions because with increasing amounts of the above the error was on the increase on the positive side. Even as low concentrations as contained in 1 ml of 0.1n solutions of these ions interfere.

There was a fair potential jump at equivalence point and well-defined potentiometric curves were obtained. Due to a reasonable potential break at equivalence point the volume consumption of the titrant could be read with great accuracy.

Tables 1 and 2 show that As(III) could be determined with reasonable accuracy, precision and rapidity in 1n hydrochloric acid using cobalt(III) acetate as titrant. The maximum relative standard deviation per cent is 1.28 when 600 μg of As(III) were estimated.

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