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Determination of Hydrazine and Sulphite in the Presence of one Another

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Abstract. A simple titrimetric method has been developed for determination of sulphite and hydrazine in compounds containing both. The sulphite is oxidized quantitatively to sulphate by iodine in acid medium, and the sum of hydrazine and sulphite is determined by Andrews titration with iodate. The hydrazine content is found by difference.

Key words: hydrazine, sulphite, iodine, iodate, oxidative.

The compounds $(N_2H_5)_2SO_3$ [1], $(N_2H_5)_2SO_3 . H_2O$ [2, 3], $N_2H_3SOON_2H_5$ [2], $MSO_3 . xN_2H_4 . yH_2O$ [4], $N_2H_2(SO_2 . N_2H_5)_2$ [5], $Ba_2(NSO_2)_2$ [5] and $Ca(N_2H_3SO_2)_2$ [1] have been synthesized and studied. The methods hitherto used for characterizing these compounds were rather time-consuming, generally involving measurement of the volume of nitrogen evolved on oxidation, followed by gravimetric estimation of the sulphate produced. For compounds containing hydrazine, the Andrews titration with iodate is generally used, but fails for the compounds listed above, since the sulphur-containing groups will also be titrated. During an investigation of the reaction between hydrazine hydrate and gaseous sulphur dioxide and of the $N_2H_4 . H_2O$-SO_2-metal ion system [6], it was found that this apparent source of error could be turned to advantage, since the sulphur species can be determined by oxidative titration with iodine under appropriate conditions, and the hydrazine content by difference from the sum of hydrazine and sulphur species determined by Andrews titration.

Experimental

Mixtures containing various known amounts of anhydrous sodium sulphite (99.98% pure) and hydrazinium sulphate (99.99% pure) were prepared.

Procedure

Estimation of S (or SO_3^{2-})

Place a known volume of standard iodine solution and 75 ml of water in a reagent bottle or stoppered flask and acidify it with 3–4 ml of 1 M hydrochloric acid. Add 0.08–0.5 g of the sample (accurately weighed), a little at a time, with constant stirring. Titrate the remaining iodine with standard thiosulphate solution. Run a blank titration with the same initial volume of iodine. Calculate the S or SO_3^{2-} content by using the relationship,

$$H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + 2\,HI$$

$$1 \text{ ml of } 0.025\ M\ I_2 = 0.802 \text{ mg of S} = 2.002 \text{ mg of } SO_3^{2-}$$

It is essential to add the sample to the iodine solution, and not vice versa. Hydrazine does not interfere with this determination if the pH of the titration mixture is in the range 1.5–4.8. Iodine oxidizes hydrazine only at pH > 7.5 [7].

Determination of hydrazine

Transfer 0.08–0.5 g of sample (accurately weighed) into a 250 ml flask or bottle having a close-fitting stopper, add 20 ml of water, 30 ml of concentrated hydrochloric acid and 5 ml of chloroform or carbon tetrachloride, and titrate with 0.025 M potassium iodate with vigorous shaking of the stoppered vessel between additions of titrant, until the organic layer is just decolorized.

The volume of 0.025 M iodate equivalent to the sulphite present is calculated by simple proportion from the volume of 0.025 M iodine consumed in the first titration, the two sample weights and the relationship

$$1 \text{ ml of } 0.025\ M\ KIO_3 = 1.603 \text{ mg of S} = 4.003 \text{ mg of } SO_3^{2-}$$

The volume of KIO_3 equivalent to the N_2H_4 present is calculated by difference. The amount of N_2H_4 is calculated from the relationship

$$1 \text{ ml of } 0.025\ M\ KIO_3 = 0.801 \text{ mg of } N_2H_4$$

Results and Discussion

The results obtained by this method for the test mixtures are given in Table 1, and are in good agreement with the amounts of sulphite and hydrazine used in preparation of the mixtures.

Table 1. Analysis of mixtures containing known amounts of $(N_2H_5)_2SO_4$ and Na_2SO_3

N_2H_4 (mg)		SO_3^{2-} (mg)	
Taken	Found	Taken	Found
17.3	17.4	29.5	29.4
25.6	25.6	46.3	46.2
36.5	36.6	63.1	62.7
48.8	48.5	80.3	80.4
71.1	71.2	108.8	108.4
88.7	88.5	163.8	164.8

To validate the Andrews titration of sulphite, tests were made with known weights of sodium sulphite, and the results are in good agreement with the expected values.

The complexes $MSO_3 . xN_2H_4 . yH_2O$, where M = Fe, Mn, Co, Ni and Zn have been synthesized and their magnetic, spectral and thermal properties studied [6]. The methods described here were used for characterization of these complexes [8] and also of a bisulphite [9], $Mg(HSO_3)_2 . N_2H_4 . H_2O$.

Both water-soluble and insoluble compounds can be characterized by this method.

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