

Titration of Polythionates by Means of a Standard Sodium Hypochlorite Solution

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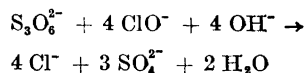
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Several titrimetric methods have been tried for the oxidation of polythionates to sulfate. Already in 1848 Gélis¹ used a standard sodium hypochlorite solution for the titration of sodium trithionate and barium tetrathionate. The polythionate solution was acidified and titrated with hypochlorite until the smell of chlorine was detectable or until indigo was decolorized. This method does not yield accurate results. Oxidation of polythionates with hypochlorite in excess in basic solution, addition of potassium iodide, acidifying, and backtitration with thiosulfate would seem a better possibility for an accurate method*.

Already Gélis¹ noticed that the oxidation of polythionates by means of hypochlorite is rather slow in basic solution, and he discarded the possibility of using the basic oxidation. Kitchener, Liberman and Spratt² have shown that basic solutions of pure hypochlorites may be boiled without decomposition. They used a solution 0.4 M with respect to sodium hydroxide and 0.1 N with respect to sodium hypochlorite, which was made by passing chlorine into the alkali until the required titre was reached. The titre of this solution was determined thiosulfatometrically, and the effect of boiling on the titre was investigated. During the first two minutes' boiling there was a loss of titre amounting to 0.7%. Thereafter the titre remained constant within 0.1% during a further 8 minutes' boiling. The initial loss was believed to be due to reaction with traces of dust. The hypochlorite solution could be kept for many months without appreciable change of titre when stored in a

dark bottle to avoid photochemical decomposition.

The present investigation deals with the problem whether it is possible to estimate the amount of tri-, tetra- and pentathionate by oxidation with an excess of sodium hypochlorite in basic solution at 100°C, addition of iodide and sulfuric acid, and backtitration with thiosulfate. In the case of trithionate the expected reaction is



and analogously for tetra- and pentathionate. As standards were used $\text{K}_2\text{S}_3\text{O}_6$, $\text{K}_2\text{S}_4\text{O}_8$ and $\text{K}_2\text{S}_5\text{O}_{10} \cdot \frac{1}{2}\text{H}_2\text{O}$, all of which correspond to the given formulae within 0.1%.

Experimental procedure. 30 ml 0.05 M sodium hypochlorite² was boiled in a flask for 3 min. To the hot solution was added 20 ml of a freshly prepared solution of the polythionate (corresponding to about 2/3 of the hypochlorite used). The mixture was heated again and allowed to boil for 30 sec. After cooling with water, 2 g potassium iodide, 10 ml 2 M sulfuric acid and 200 ml oxygen-free water were added, and the iodine formed backtitrated with standard thiosulfate using starch as indicator. The hypochlorite solution was analyzed correspondingly, i.e. was boiled for 3 min, cooled, potassium iodide and sulfuric acid added, etc.

Results. To a first approximation dithionate is not oxidized. Trithionate is not oxidized quantitatively, but only to a degree varying from 30 to 40%. Tetrathionate, however, is oxidized quantitatively (99.9, 99.8, 100.8 and 100.4% was found by experiments). Pentathionate yields results which are 1.9 to 2.2% too low. The explanation is possibly that a small percentage of dithionate is formed by the oxidation.

Conclusion. The method described yields excellent results in case of tetrathionate, whereas it cannot be used for di-, tri- and pentathionate.

1. Gélis, F. *Ann. chim. et phys.* **3** (1848) 60; *J. prakt. Chem.* **43** (1848) 449.
2. Kitchener, J. A., Liberman, A. and Spratt, D. A. *Analyst* **76** (1951) 509.

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* After the present investigation was carried out, Sharada and Vasudeva Murthy have published a paper "Oxidation of Polythionates with Chloramine-T", *Z. anal. Chem.* **177** (1960) 401.