

Estimation of Dithionate

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An improved method for the estimation of dithionate has been developed. The method is based on rapid oxidation with ammonium vanadate in a medium of hot, fairly concentrated sulfuric acid. The vanadyl ions formed are titrated with permanganate. The effects of the concentrations of sulfuric acid and of vanadate are discussed.

Quantitative determination of dithionate has always been a problem due to the exceptional stability of dithionate ions in aqueous solution. Kurtenacker *et al.*¹ describe a direct method; in earlier methods the content of dithionate has usually been calculated as a difference. Kurtenacker uses ammonium vanadate in 4 N sulfuric acid as the oxidizing agent, and he then titrates the vanadyl ions formed with permanganate. However, complete oxidation of dithionate requires at least 20 min. boiling. Vasudeva Murthy² uses dichromate in 10 N sulfuric acid as the oxidizing agent. About 1 hour's boiling is necessary to secure complete oxidation. It is further necessary to run a blank and subtract the amount of chromic ions formed. Yost and Pomeroy³ have made an investigation of the decomposition and oxidation of dithionic acid. They have measured the rate of decomposition of dithionic acid into sulfurous and sulfuric acids in the presence of various concentrations of hydrochloric acid and perchloric acid. The rate was found to be proportional to the concentration of the dithionate and to that of the total acid, provided its concentration does not exceed 0.6 N; but at higher acid concentrations the rate increases more rapidly. The rate of oxidation of dithionic acid by dichromate, bromate and iodate was found to be about the same for these three oxidizing agents, to be independent of their concentrations, and to be nearly identical with the rate of the decomposition of the acid into sulfurous and sulfuric acids. This shows that the first step in the oxidation of dithionic acid presumably is its hydrolysis, which is catalyzed by hydrogen ions.

The investigation mentioned above combined with the observed fact that moistening of a solid dithionate with conc. sulfuric acid causes immediate liberation of sulfur dioxide, led us to the conclusion that the oxidation of dithionate to sulfate by means of vanadate could be brought about in a very short time in a rather concentrated sulfuric acid solution. This turned out to be the case.

EXPERIMENTAL

As dithionate standard $\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ was used. This was controlled by igniting it to sodium sulfate (99.85 and 99.95 % was found).

A vanadate solution was made by dissolving 20 g ammonium vanadate, p.a., in a cold mixture of 40 ml conc. sulfuric acid and 190 ml distilled water. This solution is about 0.7 M with respect to vanadate.

The method used for the estimation of dithionate is as follows: *Ca.* 0.3 g of sodium dithionate dihydrate is dissolved in 5 ml of distilled water in a 300 ml Erlenmeyer flask. 7 ml of vanadate solution is added, after which 12 ml of conc. sulfuric acid is poured into the mixture. The flask is rotated a little, so that complete mixing takes place. Under these conditions (heat of mixing and considerable concentration of sulfuric acid) the oxidation is complete after 1 min. The solution is now diluted with water to *ca.* 200 ml and heated to about 50°C. It is then titrated with standard permanganate solution. Colour change from green yellow to brown yellow.

In Table 1 the first four experiments show the accuracy of the method. Expts. Nos. 5 to 12 show the influence of varying amounts of conc. sulfuric acid. It is clearly seen that a considerable volume of conc. sulfuric acid must be added to give enough heat of mixing and a fairly small concentration of water. However, 12 ml of conc. sulfuric acid is sufficient, and more than 12 ml does not seem to be of any use. If the oxidation is carried out in a 50 ml beaker, after which it is transferred into a larger flask for titration, it is sufficient with 8 ml of conc. sulfuric acid due to the smaller loss of heat to the glass. Expts. Nos. 13 and 14 are carried out in a 50 ml beaker, for which reason the error is less than in Nos. 11 and 12, which experiments are carried out in a 300 ml flask.

The necessary excess of oxidizing agent (vanadate) has also been investigated. About 100 % in excess must be present, but more in excess does not give better results.

The temperature of a vanadyl ion solution, which has to be titrated with permanganate seems to be subject to much disagreement. Czudnowicz⁴ performs the titration in hot solution, while Wegelin⁵ claims room temperature gives the best results. Rieman, Neuss and Naiman's *Quantitative Analysis*⁶ claims 50°C to be a convenient temperature of the titrand, because this temperature gives a sufficiently rapid reaction near the endpoint. This is in accordance with our experience.

It has been tried if dichromate may be used instead of vanadate. This is not the case, because a small percentage of Cr(VI) under the conditions used, will become reduced with the evolution of oxygen.

Table 1. Estimation of dithionate. For each experiment is given the weighed amount of sodium dithionate, the volume of water in which it is dissolved, the volume of vanadate solution added, the volume of conc. sulfuric acid added, the amount of sodium dithionate, which corresponds to the volume of standard decinormal permanganate used for the titration, and finally the percentage error.

Expt. No.	$\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ taken g	Water ml	Vanadate solution ml	Conc. sulfuric acid ml	$\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ found g	Error %
1	0.3090	5	7	12	0.3088	-0.06
2	0.3037	5	7	12	0.3028	-0.30
3	0.3006	5	7	12	0.2986	-0.66
4	0.3133	5	7	12	0.3125	-0.25
5	0.3057	5	7	16	0.3050	-0.23
6	0.3029	5	7	16	0.3023	-0.20
7	0.3127	5	7	10	0.3090	-1.18
8	0.3186	5	7	10	0.3183	-0.09
9	0.3086	5	7	8	0.3071	-0.49
10	0.3073	5	7	8	0.3021	-1.68
11	0.3108	5	7	6	0.2995	-3.65
12	0.3098	5	7	6	0.2984	-3.70
13	0.3494	5	7	6	0.3435	-1.69
14	0.3099	5	7	6	0.3061	-1.23

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Received January 23, 1961.