2. *A New Volumetric Method for the Estimation of Dithionates.*

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THE surprising stability of dithionates in the presence of acids and of oxidising agents renders their estimation difficult. A gravimetric method involving fusion with a large excess of alkali nitrate was proposed by Baubigny (*Compt. rend.*, 1909, **149**, 1069; see also Müller, *Bull. Soc. chim.*, 1916, **19**, 8), and volumetric methods, involving the distillation either of sulphur dioxide or of bromine, were suggested by Ashley (*Amer. J. Sci.*, 1906, **22**, 259), Fischer and Classen (*Z. angew. Chem.*, 1922, **35**, 198), and Mayr and Szentpaly-Peyfuss (*Z. anorg. Chem.*, 1924, **131**, 203). A rapid process for estimating dithionate was required and, since the published methods were tedious and did not readily give reliable results, a new method has been devised which is both rapid and accurate.

Yost and Pomeroy (*J. Amer. Chem. Soc.*, 1927, **49**, 703) found that the rate of oxidation of a dithionate in acid solution is almost independent of the concentration or nature of the oxidising agent ($K_2Cr_2O_7$, $KBrO_3$, or KIO_3), but probably depends on the rate of decomposition of the dithionic acid into sulphuric and sulphurous acids, which is catalysed by strong acids. It appeared possible, therefore, that by boiling a dithionate with a strongly acidified solution of dichromate quantitative oxidation to sulphate would occur: $Cr_2O_7'' + 3S_2O_6'' + 2H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 6SO_4'' + H_2O$. Since the dichromate is stable and non-volatile, its decrease of concentration, determined iodometrically, should be a measure of the dithionate originally present. This possibility has been tested and found to provide a basis for a new volumetric method of estimating dithionates.

The following is a typical example of the procedure adopted. To 25 c.c. of a 0·0125*M*-solution of $Na_2S_2O_6,2H_2O$, prep. by Baubigny's method (*Compt. rend.*, 1910, **150**, 466) and checked by gravimetric analysis (Baubigny, *ibid.*, 1909, **149**, 1069), were added 10 c.c. of 0·025*M*-$K_2Cr_2O_7$ and 10 c.c. of approx. 10*N*-H_2SO_4; the mixture was boiled for 1 hr., H_2O being added from time to time to replace loss by evaporation. After cooling, 5 c.c. of 10% KI aq. were added and the liberated I was titrated with $Na_2S_2O_3$, starch being used as indicator; no difficulty was experienced in obtaining a sharp end-point. In two expts., 17·52 and 17·49 c.c. of $Na_2S_2O_3$ aq. were used; mean = 17·51 c.c. The 10 c.c. of 0·025*M*-$K_2Cr_2O_7$ required 30·01 c.c. of the $Na_2S_2O_3$ aq.; hence the S_2O_6'' present in 25 c.c. of the solution used = 12·50 × 10·0/30·01 c.c. of 0·025*M*-$K_2Cr_2O_7$. The concn. of the S_2O_6'' solution is thus found to be 0·0125*M*, in exact agreement with the actual value.

If it is required (cf. Haber *et al.*, *Ber.*, 1932, **65**, 729; *Z. physikal. Chem.*, 1932, *B*, **18**, 103) to analyse mixtures of SO_3'' and S_2O_6'', the former may be removed by boiling with dil. (approx. 0·5*N*) AcOH for about 15 min., and the S_2O_6'' then determined by the method described. The AcOH must be freed from oxidisable impurities by distillation from CrO_3. The SO_3'' in the mixture may be estimated by allowing the standard $K_2Cr_2O_7$ aq. to liberate I from KI in the cold and adding the mixture to be analysed; the excess I is titrated with $Na_2S_2O_3$. Under these conditions the SO_3'' only is oxidised and the S_2O_6'' remains unattacked. The method has been found satisfactory for a number of mixtures of SO_3'' and S_2O_6''; in addition to its simplicity, it has the merit of requiring only one standard solution, *viz.*, $K_2Cr_2O_7$.

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