197. *The Estimation of Sulphur Trioxide in its Mixtures with Sulphur Dioxide by the Method of Amperometric Titration.*

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The method of amperometric titration has been used to determine the sulphur trioxide content of sulphur dioxide–sulphur trioxide mixtures in which the proportion of the latter is about 2% of the whole. The gases were absorbed in N-sodium hydroxide, followed by acidification and removal of sulphur dioxide by a current of nitrogen, with glycerol in the solution to inhibit oxidation of the sulphite. The sulphate solution was then neutralised and titrated amperometrically with lead nitrate solution using a simple type of polarograph.

In the course of investigations on the oxidation of sulphur dioxide in flue gases, it was necessary to develop a method of estimation of the sulphur trioxide in a system which contained a large excess of the dioxide (SO_2/SO_3 of the order 50 : 1). The dioxide in such a mixture may readily be determined by iodometric titration, but the determination of the trioxide presents considerable difficulties.

The only available alternative to the usual gravimetric methods is due to Taylor and Johnstone (*J. Ind. Eng. Chem. Anal.*, 1929, **1**, 197), depending on the filtration of the trioxide mist through a fine-grain alundum crucible. Another method, utilising the principle of amperometric titration, after absorption of the gases in sodium hydroxide, is described below and has been found to give good results.

Although a sulphur trioxide mist is difficult to absorb in water, it has been found possible to obtain complete dissolution of it by bubbling the gases through N-sodium hydroxide.

Experimental.

Determination of Sulphate by Amperometric Titration.—A full description of this mode of use of the polarograph is given in " Polarography " (Kolthoff and Lingane, Inter-Science Pub. Inc., 1941).

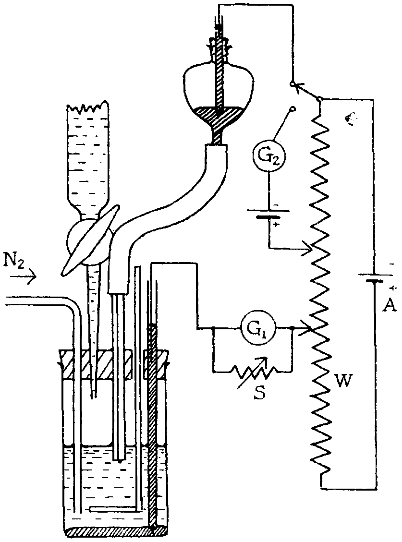
A. *Apparatus.*—A simple form of polarograph was employed (see Fig. 1). The cell was a glass beaker of about 100 c.c. capacity with a shallow pool of mercury as anode, and the dropping-mercury electrode consisted of a piece of carefully cleansed thermometer tubing, the rate of fall being adjusted to give one drop in about three seconds. The top of the cell was closed by a rubber stopper through which passed the capillary tube, the tip of the burette, the inlet tube for a stream of inert gas, and a hole for a glass stirrer. The potential applied to the cell was obtained from a potentiometer box *P*, connected to a 2-volt accumulator *A*, with the cell in series with the galvanometer G_1, shunted by a variable resistance *S*. The potentiometer box was standardised by a Weston cell *W*, and the applied potential to the cell measured by the setting of the box. The galvanometer G_1 was a Cambridge moving-coil instrument with lamp and scale, and a sensitivity of about 1 cm. scale division per microamp. It was used to obtain the current through the cell, with the shunt *S* at a suitable value. The absolute value of the current need not be known, since relative changes only are required.

B. *Choice of Precipitant.*—Two suitable cations were available : barium (solubility of sulphate, 0·24 mg./100 g. H_2O at 20°; half-wave potential in neutral solution, −1·95 volts) and lead (solubility of sulphate, 4·1 mg./100 g. H_2O at 20°; half-wave potential in neutral solution, −0·41 volt).

(1) *Use of barium.* Of these two, barium appeared the more suitable since its sulphite is considerably more soluble

than its sulphate (20 mg./100 g. H_2O at 20°), and it was considered that this might permit of the titration of the sulphate in the presence of an excess of sulphite solution, whereas the possibility does not exist with lead, which has a very insoluble sulphite. Estimations of sulphate with barium by this method have already been performed by Heyrovský and Berezický (*Coll. Czech. Chem. Comm.*, 1929, **1**, 19) and by Majer (*Z. Elektrochem.*, 1936, **42**, 120). It was unsuitable, however, in the present work for the following reasons. First, the half-wave potential of barium lies close to those of sodium and potassium, the hydroxides of which in fairly concentrated solution would be necessary for the absorption of the gases, and it was difficult to separate their diffusion currents from that of barium; and secondly, direct titrations of N/100-barium chloride gave end-points which were too high by 10—20%, which was considered to be due to the absorption of barium chloride on the precipitated sulphate. It was therefore decided to use lead.

FIG. 1.



Polarograph cell and circuit.

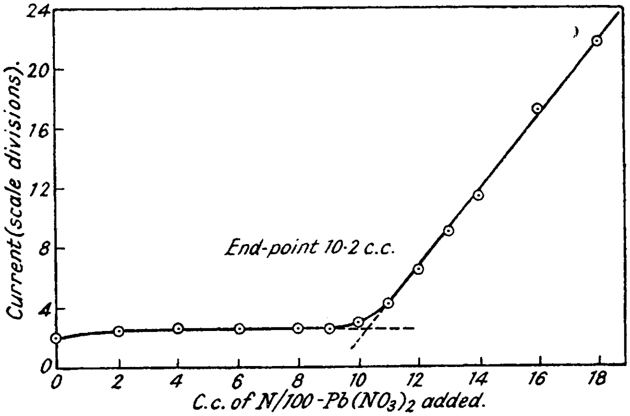
(2) *Use of lead.* The use of lead nitrate as a precipitant for sulphate demands the removal of the sulphite because of its high insolubility. It has been used as an amperometric reagent for sulphate by Majer (*loc. cit.*) and by Kolthoff and Pan (*J. Amer. Chem. Soc.*, 1940, **62**, 3332), and has been found to be satisfactory under the conditions used in the present work, as follows: (i) The titration is carried out in presence of ethyl alcohol, as recommended by Spalenka (*Coll. Czech. Chem. Comm.*, 1939, **11**, 146), to reduce the solubility of lead sulphate. (ii) Addition of solid lead sulphate to prevent supersaturation. (iii) Addition of a small quantity of methyl-orange to suppress polarographic current maxima. (iv) Potassium salts may not be used as ground electrolytes since low end-points are obtained owing to precipitation of a double potassium lead sulphate. Hence in the absorption of the gases it was necessary to use sodium hydroxide.

A typical result is shown in Fig. 2. The titrations were carried out in an atmosphere of nitrogen, and the potential of the cathode was set at −0·8 volt, *i.e.*, well above the half-wave potential of lead in neutral or acid solution. The accuracy with solutions of concentrations of the order of N/100 was within about 2%.

It was found sufficient to use a large pool of mercury as anode (area about 12 sq. cm.) since, according to Majer (*loc. cit.*), if the current density is small, it is practically unpolarised, even in nitrate and sulphate solutions. Since Kolthoff and Pan (*J. Amer. Chem. Soc.*, 1939, **61**, 3402) note that a slight polarisation of the anode does not affect the results of amperometric titrations, it was found more convenient to use this very simple form of anode rather than the standard calomel electrode required when an accurate knowledge of the potential of the cathode is desired. All the solutions used were made up with distilled water which had been freed from dissolved air and carbon dioxide by boiling.

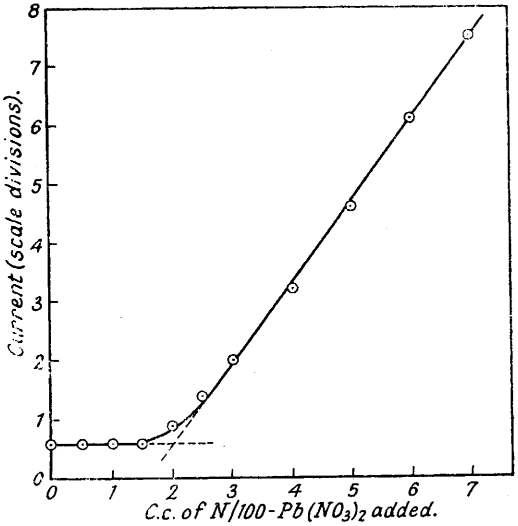
Procedure for Sulphate–Sulphite Solutions.—A series of experiments using solutions of known sulphate content was next undertaken. If the original dioxide and trioxide are absorbed in N-sodium hydroxide a typical resulting solution would be represented by: NaOH(~N), Na_2SO_4(~N/200), Na_2SO_3(~N/10). Test solutions of this order of concentration were made by using sulphate in known amount and passing sulphur dioxide into the solution from a syphon. The solution was acidified with N-nitric acid. A few drops of glycerol were added to the alkali in the first place to inhibit oxidation of sulphite in solution. The dioxide was then blown out by passing a stream of nitrogen for 30 minutes, and the solution then rendered just alkaline to methyl-orange by addition of N-sodium hydroxide, and titrated with N/100-lead nitrate as previously.

FIG. 2.



5*C.c.* N/50-H_2SO_4 + 5 *c.c.* N-NaOH *neutralised with* N-HNO_3 (*methyl-orange indicator*) + 5 *c.c. ethyl alcohol* + *solid lead sulphate. Cathode potential* — 0·8 *volt. Nitrogen passed for* 2 *mins. after each addition of* $Pb(NO_3)_2$.

FIG. 3.



5*C.c. of solution* A + 10 *c.c.* N-HNO_3 + 5 *c.c. ethyl alcohol. Nitogen passed for* 45 *mins.* N-NaOH *added until just alkaline to methyl-orange. Titrated with* N/100-$Pb(NO_3)_2$ *solution. Cathode potential* —0·8 *volt. Nitrogen blown for* 2 *mins. after each addition of* $Pb(NO_3)_2$.

A convenient check on the complete removal of dioxide was available since this substance in acid solution gives a diffusion current at $-0{\cdot}3$ volt. The absence of such a current at the P.D. used for the titration ($v_1 = -0{\cdot}8$ volt = applied potential) was taken to indicate complete removal. The solution was arranged to be about neutral since lead hydroxide (solubility = 15·5 mg./100 g. H_2O at 20°) is liable to be precipitated in alkaline solution, and since at the potential employed an appreciable hydrogen-ion concentration might have yielded a sufficient diffusion current to interfere with the titration.

The end-points corresponded to the original sulphate concentration with an accuracy of within 2%, thus showing that the glycerol added effectively inhibited the oxidation of sulphite in the solution.

Comparison with Gravimetric Estimation of Sulphate.—A final test of the amperometric method was obtained by analysing a sulphate–sulphite solution of unknown sulphate concentration both amperometrically and gravimetrically. Sulphur dioxide from a gas-burette was passed through a vertical Pyrex tube containing pure concentrated sulphuric acid kept at about 280° by means of an external heating coil. Arrangement was made for the passage of the same specimen of dioxide through the hot acid several times in order to pick up sufficient sulphuric acid. The resulting mixture of gases was absorbed in a further gas-burette containing a known volume of N-sodium hydroxide with a little glycerol and methyl-orange present. The solution was divided into two portions A and B.

Analysis of A. A polarographic estimation as previously described was performed after removal of the dioxide from the solution by a stream of nitrogen (see Fig. 3).

Analysis of B. The solution was acidified with hydrochloric acid and the dioxide blown out by a stream of nitrogen for an hour. A solution of N/5-barium chloride was then added dropwise to the boiling solution until the precipitation was complete. The barium sulphate was filtered off, washed, and dried in the usual way.

Results.	Amperometric.	Gravimetric.
Normality of sulphate solution	0·0057	0·0059
	0·0040	0·0038

The accuracy of these results justifies the application of the method to the determination of the trioxide in presence of the dioxide, provided suitable absorption can be obtained. An amperometric titration can be performed in about an hour, which represents a considerable saving of time on the gravimetric method.

Procedure for Gaseous Mixtures.—N-Sodium hydroxide has been found to be a suitable absorbent which does not interfere with the later polarographic analysis. The absorption was carried out by bubbling the gas at a known rate through the alkali in a specially constructed wash-bottle containing 10 c.c. of solution with glycerol and methyl-orange, and fitted with a burette tap at the base for withdrawal. The height of the liquid column was about 8 cm.

A test of the efficiency of this arrangement was made by running two of them in series. There was never any detectable sulphate in the second bottle whereas the order of concentration in the first was N/200-sulphate. The smallest concentration detectable by this method was about N/5000, so the first wash-bottle appeared to have effectively absorbed the trioxide. The solution from the wash-bottle was run out directly into the polarograph cell containing excess of N-nitric acid, and removal of the dioxide commenced at once by blowing nitrogen through. Hence the solution was never exposed for an appreciable time to the air. Titration, as above, was carried out with N/50-lead nitrate.

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