ACTA CHEMICA SCANDINAVICA 3 (1949) 773—777

Determination of Sulphate by Reduction with Stannous Chloride

E. RANCKE-MADSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

Methods for the determination of sulphate by reduction to hydrogen sulphide have previously been worked out. These methods have been substantially based on dry heating or fusion of the sulphate containing substance with adequate reductants. Kurtenacker [1] gives a survey of these methods, and later sodium as well as potassium has been used as a reductant in a micromethod by Bürger [2].

In the following a method will be described in which the sulphate is reduced in solution. The principle of the method is as follows: The wellknown fact that hot concentrated sulphuric acid is a rather powerful oxidant is utilized by adding the sulphate containing solution to an acid of a high boiling point, in this case phosphoric acid, and boiling down after further addition af an adequate reductant. Investigation of diverse reductants is now beeing carried out, and in the present paper stannous chloride as a reductant will be dealt with. Experiments have shown that, when a solution of sodium sulphate, stannous chloride and phosphoric acid is boiled down, all sulphate present will be reduced. Most of the sulphate will be reduced to hydrogen sulphide, but a small percentage will only be reduced to sulphur dioxide. If the hydrogen sulphide and sulphur dioxide formed are absorbed (in carbon dioxide atmosphere) in iodine solution, the following reactions will take place:

$$H_2S + I_2 \rightarrow S + 2I^- + 2\ H^+$$

and

$$SO_2 + I_2 + 2\ H_2O \rightarrow SO_4^{--} + 2\ I^- + 4\ H^+$$

i. e. that each sulphur atom requires two iodine atoms, and the iodine in excess can be titrated with standard thiosulphate. (In some experiments with absorption of the reduced sulphur compounds in a cadmium acetate buffer, in which only the hydrogen sulphide was absorbed quantitatively, the results found were 2—3 % too low.)

When a quantitative reduction of the sulphate shall take place, a rather large excess of stannous chloride must be used. When up to 0.1 g SO_4 is present, about 4 g of cryst. stannous chloride is used.

When the absorption of hydrogen sulphide in iodine solution takes place, a) the hydrogen sulphide must be absorbed quantitatively, and b) the iodine must be prevented from escaping together with the carbon dioxide current.

a) The quantitative absorption is obtained in an absorption tube provided with ten bulbs (Fig. 1). Into this tube 1) 25 ml standard potassium iodate solution (about 0.1 N) is pipetted off; furthermore 2) 2 g cryst. potassium iodide, 3) 10 ml 2 % cadmium sulphate solution, and 4) 10 ml 2 M sodium hydroxide solution are added. When boiling down the solution of sodium sulphate, stannous chloride and phosphoric acid about 0.035 mole hydrochloric acid is expelled from 4 g stannous chloride. This hydrochloric acid imparts to the basic iodate-iodide solution a suitable acidity, so that the later formed hydrogen sulphide is absorbed quantitatively, when cadmium salt is present. Without cadmium sulphate present in the absorbing solution or when this solution was considerably more acid, it was ascertained, that some hydrogen sulphide escaped. As an extra measure of precaution the carbon dioxide, which had passed the absorbing solution, was allowed to bubble through a solution, contained in a glass cylinder, and consisting of 10 ml 2 % cadmium sulphate solution, 1 g potassium iodide and 15 ml water, but in none of the later described experiments did hydrogen sulphide reach the cylinder. The addition of cadmium sulphate to the solution in the cylinder is consequently unnecessary.

b) To prevent a loss of iodine from the absorbing solution — due to the carbon dioxide current — a rather large excess of potassium iodide was added to that solution, and further the absorption tube was water-cooled. As already mentioned the carbon dioxide was finally allowed to bubble through a solution of 1 g potassium iodide in 25 ml water in a cylinder. In the experiments a slight amount of iodine was found in the cylinder (corresponding to about 0.05 ml 0.1 N iodine solution), and blank tests carried out later (see below) seem to indicate that about just as much iodine nevertheless escaped.

The experimental set-up appears from Fig. 1. The stoppers used were made of rubber. The absorption tube is protected against heat from the burner by means of a sheet of asbestos board.

The reduction of the sulphate was carried out in a 100 ml longnecked Kjeldahl flask. In this flask was placed 1) a small shard of porous porcelain, 2) 4 g stannous chloride ($SnCl_2,2H_2O$), 3) the sample (in the experiments mentioned a solution of sodium sulphate) washed down with water (the volume of sample plus water was about 20 ml), and 4)

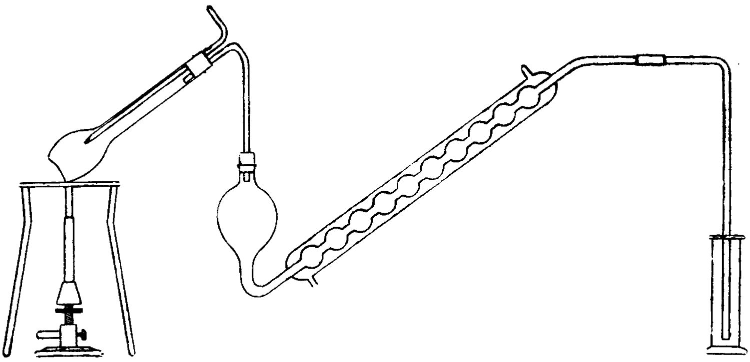

Fig. 1. Experimental set-up for reduction of sulphate with stannous chloride and following absorption of the reduced sulphur products.

10 ml conc. phosphoric acid (85 %). (After completing the experiment the flask is rinsed with cold water and boiled out with water; finally some sodium hydroxide solution is boiled in the flask.)

Into the absorption tube is 1) standard potassium iodate solution (about 0.1 *N*) pipetted off; further 2) 2 g potassium iodide, 3) 10 ml 2 % cadmium sulphate ($CdSO_4$, $\frac{8}{3}H_2O$), and 4) 10 ml 2 *M* sodium hydroxide are added.

In the cylinder was placed 1) 10 ml 2 % cadmium sulphate, 2) 1 g potassium iodide, and 3) 15 ml water.

The current of carbon dioxide was produced by a carbon dioxide pressure cylinder and the rate was 60—80 ml per min.

The heating of the Kjeldahl flask was done by a heavy duty Bunsen burner.

An experiment progresses as follows: After a little less than 3 min the mixture in the flask begins boiling. Before starting the experiment a white precipitate of cadmium hydroxide in a colourless liquid is seen in the absorption tube. Gradually as the carbon dioxide bubbles through this suspension, the liquid will assume a yellowish colour. About 10 min after the boiling has begun, considerable amounts of hydrochloric acid distills over in the absorption tube, so that the liquid becomes redbrown due to triiodide ions, coincident with the precipitate starting to dissolve. After the elapse of a further 4—5 min the beginning of a precipitate of sulphur is seen in the absorption tube, and from now on heating is continued 4—5 min until the mixture in the Kjeldahl flask is quite opaque due to a white precipitate. (This precipitate is not formed — or at least only to a slight degree — in the blank tests later mentioned, or if the analysis contains only small amounts of sulphate.)

A little more than 20 min have now elapsed since the Bunsen burner was lighted, and the gas is at this point turned off, whereas the carbon dioxide current is continued for 20 min. Hereafter the contents of the absorption tube and the cylinder are washed quantitatively over into a 500 ml Erlenmeyer flask, and the excess of iodine is titrated with standard sodium thiosulphate.

The whole determination can — when the required solutions are at hand — be carried out in one hour.

In the experiments carried out in this work a solution of sodium sulphate, containing 1.349 % SO_4 is used as sample. This solution is controlled gravimetrically as barium sulphate and by evaporation as sodium sulphate.

The 25 ml potassium iodate solution used in each experiment required, by direct titration, 24.92 ml 0.1008 *N* sodium thiosulphate. Further some blank tests are run by adding 20 ml water in stead of the sample plus washing water. In these blank tests titration of the 25 ml potassium iodate required on an average 24.82 ml sodium thiosulphate. However it is worth mentioning that while it was impossible in a real analysis to detect loss of iodine by placing a piece of potassium iodide-starch filter-paper above the mouth of the cylinder, a faint blue colour could be seen when carrying out the blank tests. This seems to indicate that the blank value 0.10 ml thiosulphate is too large, which is also rather likely, because a carbon dioxide current was bubbled through a solution containing 25 ml 0.1 *N* iodine for about 30 min. while — in a real experiment — the 25 ml 0.1 *N* iodine was only present for about 5 min, and about 5 ml 0.1 *N* iodine was present for about 25 min.

The experimental results are given in Table 1. In the last few experiments the error of the determination is of course increased due to the smaller amount of sodium sulphate solution used.

Table 1. Determination — by reduction with stannous chloride — of sulphate in a sodium sulphate solution which contains 1.349 % SO_4. The standard thiosulphate used is 0.1008 N. (A) are values without regard to the blank value; (B) are the values corrected for the blank value.

Sample g	Titration of the excess of iodine Thiosulphate used, ml	Consumption of KIO_3 recalculated to ml thiosulphate (A)	(B)	% SO_4 found (A)	(B)
7.0377	5.26	19.66	19.56	1.353	1.346
7.0052	5.37	19.55	19.45	1.352	1.344
7.0779	5.14	19.78	19.68	1.353	1.346
7.1805	4.88	20.04	19.94	1.351	1.344
7.2418	4.68	20.24	20.14	1.353	1.346
7.9921	2.59	22.33	22.23	1.353	1.346
6.0305	8.02	16.90	16.80	1.357	1.348
5.0050	10.86	14.06	13.96	1.360	1.351
4.0766	13.44	11.48	11.38	1.363	1.352
3.0632	16.25	8.67	8.57	1.370	1.355

The mean values of the first six experiments, in which 7—8 g sodium sulphate solution is used, are respectively (A) 1.353 % SO_4 and (B) 1.345 % SO_4. If we assume a blank value half of that found in the blank tests (see above), the results would agree perfectly with the value 1.349 % SO_4, found by other methods. If we do not make this assumption the results are 3 ‰ too high without taking the blank value into consideration, and 3 ‰ too low when we do take the blank value into consideration.

In the experiments mentioned only pure sodium sulphate solutions have been analyzed. It is likely that the presence of diverse compounds will complicate or even forbid the use of the method here described. Investigations of these problems will be continued. The possibility of using this method for sulphur determination in other sulphur compounds will also be investigated.

SUMMARY

A determination of sulphate in a sodium sulphate solution is carried out by reduction with stannous chloride in a solution acidified with phosphoric acid — and a following iodometric determination.

REFERENCES

1. Kurtenacker, A. *Analytische Chemie der Sauerstoffsäuren des Schwefels.* Stuttgart (1938).
2. Bürger, K., *Angew. Chem.* 54 (1941) 479, *Die Chemie* 55 (1942) 245.

Received June 2, 1949.