

Determination of Sulphate by Reduction with Stannous Chloride. II

E. RANCKE-MADSEN and
H. THEILGAARD-MADSEN

Chemistry Department A, Danish University
of Technology, Copenhagen, Denmark

In a previous paper¹ was shown that sulphate may be determined by reduction with stannous chloride, when a solution of sodium sulphate, stannous chloride and phosphoric acid is boiled down.

By checking the method with another apparatus but the same experimental set-up, it proved convenient to heat the reacting mixture a little more cautiously and to reduce the rate of the current of carbon dioxide. Otherwise there seemed to be a tendency to attain an incomplete absorption of the hydrogen sulphide formed.

Nitric acid present. As to be expected the presence of nitric acid prohibited the method. However, experiments have shown that the determination could be carried out to complete satisfaction, when the nitric acid was removed by boiling down with phosphoric acid before the stannous chloride was added.

Mercury salts present. As to be expected the method failed, when mercury salts were present in the sample.

Barium salts present. A standard solution of sodium sulphate containing 1.336% SO_4 was used in the following experiments. This solution was controlled gravimetrically as barium sulphate and by evaporation as sodium sulphate.

Introductory experiments were carried out as follows: Barium chloride in excess was added to a weighed portion of the sodium sulphate sample, and the mixture was evaporated towards dryness. Now 1) 20 ml water, 2) 4 g stannous chloride, and 3) 10 ml phosphoric acid (85%) were added. However, the method could not be carried through to satisfaction (and the

Table 1. Determination — by reduction with stannous chloride — of sulphate in a sodium sulphate solution which contains 1.336% SO_4 . Before the reduction an excess of barium chloride was added. The mentioned volumes of sodium thiosulphate solution and potassium iodate solution are recalculated to 0.1000 N.

Sample g	$\text{Na}_2\text{S}_2\text{O}_3$ ml	KIO_3 ml	% SO_4 found
6.7692	6.07	18.91	1.342
6.8949	5.75	19.23	1.340
6.9159	5.68	19.30	1.340
7.6388	3.66	21.32	1.341
7.3163	4.53	20.45	1.343
6.1333	7.81	17.17	1.345
6.1246	7.84	17.14	1.344
6.2188	7.63	17.35	1.340
6.1162	7.91	17.07	1.341

results were a few percent too low), because an almost solid mass was formed. Therefore the method was altered: 20 ml phosphoric acid was used (instead of 10 ml), and then the reduction was carried through without difficulty and in usual time.

The experimental results are given in Table 1. It may be added that no loss of iodine, caused by the carbon dioxide current, could be detected, and the results were not corrected for an eventual loss of iodine (see previous paper¹). The mean value was 1.342% SO_4 in good accordance with the 1.336% SO_4 . If we assume that the results are 3% too high (due to loss of iodine), we get the corrected value 1.338%.

When carrying out the reduction of the slightly soluble barium sulphate it was seen that the reacting mixture gradually became completely limpid which showed that the precipitated sulphate was now reduced. A few experiments were interrupted when the reacting mixture had just become limpid, and it was found that hydrogen sulphide corresponding to 1.315 and 1.318% SO_4 had distilled over. If the remains of hydrogen sulphide have to be forced over into the iodine solution, the boiling must be continued as described in the earlier published method.

Table 2. Determination — by reduction with stannous chloride and simultaneous presence of cupric oxide — of sulphate in potassium sulphate pro analysi. 20.00 ml about 0.1 N potassium iodate solution were used in each of the first 6 experiments and 50.00 ml in each of the last 3 experiments. The volumes of potassium iodate solution are recalculated to 0.1000 N.

K ₂ SO ₄ weighed g	KIO ₃ ml	K ₂ SO ₄ found g
0.1069	12.19	0.1062
0.1114	12.78	0.1114
0.1126	12.96	0.1129
0.1064	12.11	0.1055
0.1072	12.33	0.1074
0.1115	12.76	0.1112
0.3449	39.59	0.3450
0.3080	35.18	0.3065
0.3062	35.18	0.3065

Presence of other elements which form slightly soluble sulphates. In the same way as mentioned in the previous section, it was investigated if presence of calcium or lead influenced the method. This was not the case. It may be added that the presence of lead never caused formation of visible lead sulphide in the boiling flask.

Presence of elements which form slightly soluble sulphides. An example of such an element is lead which is mentioned above. Further it was tried to add copper salts: To the weighed sample was added about 0.5 g of diverse copper salts. Surprisingly, it now appeared that no hydrogen sulphide distilled over, but sulphur dioxide only, though copper sulphide was formed as an intermediate in the boiling flask.

This fact led up to the possibility of altering the earlier published method so that sulphur dioxide only is produced by the reduction of sulphate. The following method was tried with a favourable result: To a weighed portion of the sample were added 1) 4 g stannous chloride, 2) 1 g large-grained cupric oxide, and 3) 20 ml phosphoric acid (85%). An ordinary Bunsen burner was used for heating. Further 1) standard potassium iodate solu-

tion (about 0.1 N) was pipetted off into the absorption system, and 2) 2 g potassium iodide, and 3) 10 ml 2 M sodium hydroxide were added. According to this method the sulphate content in potassium sulphate pro analysi was determined; the results are given in Table 2.

Introductory experiments indicate that sulphate may be determined also by boiling down with phosphoric acid using cuprous chloride or zinc as reductant. Investigations of these problems will be continued.

1. Rancke-Madsen, E. *Acta Chem. Scand.* **3** (1949) 773.

Received October 12, 1951.

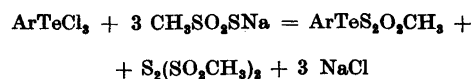
Tellurenyl Sulphur Compounds

OLAV FOSS

*Universitetets Kjemiske Institutt,
Blindern — Oslo, Norway*

Whereas sulphenyl and selenenyl compounds, with the formulae RSX and RSeX where X is an electronegative atom or group, are well known¹⁻⁴, no tellurenyl compounds, RTeX, have been described in literature. We wish to report the syntheses of the first types of tellurenyl compounds, *viz.*, some *p*-methoxybenzenetellurenyl pseudohalides.

p-Anisyl telluritrichloride⁵ reacts with sodium methanethiosulphonate to give *p*-methoxybenzenetellurenyl methanethiosulphonate:



The following procedure was employed: 6.8 g (0.02 mole) of *p*-anisyl telluritrichlor-