

337. *The Estimation of Sulphur in Organic Compounds.*

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It is well known that the estimation of sulphur by the Carius method in certain types of organic substances, *e.g.*, sulphones, may lead to low results owing to incomplete oxidation. In fusion methods there is the additional risk of loss by volatilisation. The following method, in which the nickel crucible of Asboth (*Chem.-Ztg.*, 1895, **19**, 2040) is replaced by a nickel "test-tube," is rapid and gives accurate results both with difficultly oxidisable substances and with liquids even as volatile as ethyl mercaptan.

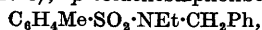
Approx. 0.2—0.3 g. of the substance is introduced into a weighed Ni tube closed at one end, 18 cm. long and of 2 cm. internal diameter, and the tube reweighed. If the substance is a liquid, it should be introduced by means of a suitable pipette controlled by a rubber teat, care being taken that no liquid is allowed to touch the side of the tube. About 5 g. of the fusion mixture (equal parts of pure Na_2O_2 and anhyd. Na_2CO_3) are mixed with the substance by means of a thin nickel or glass rod. The mixture, occupying about 2 cm. of the tube, is covered with about 20 g. of the same oxidising mixture, occupying a further 8 cm. of the tube, the last portion being used for the "rinsing" of the nickel rod. The tube is tapped while in an upright position so that the mixture settles with no air channels. It is then clamped at an angle, and the centre of the tube, containing the upper 5 cm. of Na_2O_2 mixture, is heated. When this part of the tube has just commenced to glow, the lower part is also heated, at first gently and then more strongly until the tube is at a dull red heat and the contents molten, in which state the tube is kept for 5 mins. The burners are then removed and, while still hot, the tube is inclined nearly to a horizontal position so that the melt runs up the inside of the tube and its solution at a later stage is facilitated. After cooling, the contents of the tube are dissolved by repeated extraction with hot H_2O and finally by means of a little warm dil. HCl aq. The solution, still alkaline, is transferred to a large Ni crucible (a glass beaker should not be used unless precautions are subsequently taken to avoid separation of hydrated SiO_2), where it is treated with excess Br aq. and heated for 15 mins. on the steam-bath. The product is then cooled, filtered, acidified with HCl aq., boiled, and pptd. with BaCl_2 in the usual way.

Substances which inflame spontaneously in contact with Na_2O_2 (*e.g.*, diethyl sulphide, ethyl mercaptan) should be mixed with about 3 g. of Na_2CO_3 prior to the addition of the oxidising mixture.

By heating the upper end of the tube first, any vapours coming from the bottom of the tube pass through a layer of heated Na_2O_2 mixture and are completely oxidised.

The following results, showing the percentage of S found (the theo. values are in parentheses), are typical: ethyl mercaptan, Et-SH, 51.2 (51.6); diethyl sulphide, Et_2S , 35.2 (35.5); monothioethyleneglycol, $\text{CH}_2(\text{SH})\cdot\text{CH}_2\cdot\text{OH}$, 41.1 (41.0); ethyl benzenesulphonate, $\text{Ph}\cdot\text{SO}_3\text{Et}$, 17.2 (17.2); $\beta\beta'$ -dichloro-

diethyl sulphide, $S(CH_2 \cdot CH_2Cl)_2$, 20.2 (20.2); $\beta\beta'$ -dihydroxydiethyl sulphide, $S(CH_2 \cdot CH_2 \cdot OH)_2$, 26.1 (26.2); *p*-toluenesulphonbenzylethylamide,



11.1 (11.1); *p*-nitrobenzyl *p*-toluenesulphonate, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot O \cdot SO_2 \cdot C_6H_4Me$, 10.6 (10.4); diphenylsulphone, Ph_2SO_2 , 14.6 (14.7); sulphonal, $Me_2C(SO_2Et)_2$, 28.4 (28.1).

In successive analyses of *p*-toluenesulphonbenzylethylamide by the Carius method (12 hrs.' heating with fuming HNO_3 at 300°), the results were S, 9.3, 9.8%.

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THE RESEARCH ESTABLISHMENT,
SUTTON OAK.

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