

A solution of the isothiocyanate (250 mg) and benzylamine (400 mg) in ether (5 ml) rapidly deposited the crystalline (*S*)-1-benzyl-3-(*a*-methylbenzyl)-thiourea. Two recrystallizations from aqueous ethanol afforded colourless needles (267 mg), m. p. 82.5°, $[\alpha]_D^{24} + 22.8^\circ$ (c 2.4, 96% EtOH). (Found: C 71.40; H 6.71; N 10.20. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36). The UV-spectrum in ethanol displayed a maximum at 243 $m\mu$ (ϵ 14 800), a minimum at 238 $m\mu$ (ϵ 14 100), and strong end-absorption towards the short wave-length region.

R(-)-*a*-Methylbenzyl isothiocyanate (II). This mustard oil was prepared from (+)-*a*-methylbenzylamine ($[\alpha]_D^{24} + 38.9^\circ$ (neat)) in exactly the same way, b. p. 121° at 10 mm, n_D^{25} 1.5801; $[\alpha]_D^{24} - 17.3^\circ$ (c 10.0, $CHCl_3$). (Found: C 66.15; H 5.44; N 8.68. Calc. for C_9H_9NS : C 66.24; H 5.56; N 8.59).

Upon reaction of the mustard oil with benzylamine the (*R*)-1-benzyl-3-(*a*-methylbenzyl)-thiourea was obtained, m. p. 82.5°, $[\alpha]_D^{24} - 23.4^\circ$ (c 2.3, 96% EtOH). (Found: C 71.05; H 6.63; N 10.36. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36).

(±)-*a*-Methylbenzyl isothiocyanate. Racemic *a*-methylbenzylamine was transformed into the corresponding isothiocyanate according to the directions given by Schmidt *et al.*³ for the preparation of analogous compounds. The yield of pure mustard oil, b. p. 122–123° at 12 mm, was 55%; n_D^{25} 1.5801. (Ref.²: b. p. 135–137°/23 mm, 133–134°/20 mm; n_D^{25} 1.5784, 1.5780).

The racemic 1-benzyl-3-(*a*-methylbenzyl)-thiourea separated in colourless needles from aqueous ethanol, m. p. 100°. (Found: C 71.35; H 6.62; N 9.98. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36).

The oily thiourea, resulting from the reaction of the isothiocyanate with ammonia, was subjected to paper chromatography in water-saturated chloroform according to our usual method⁸. An R_{Fh} -value of 1.15 was determined, *i. e.* the compound migrates at a rate definitely higher than that of control spots of benzyl- (R_{Fh} 0.93) and the isomeric β -phenylethyl-thiourea (R_{Fh} 1.03).

Microanalyses were made in this laboratory by Mr. P. Hansen. The experimental assistance of Mr. R. Boe Jensen is acknowledged. Dr. Egelund Pedersen of this laboratory kindly furnished the optically pure *a*-methylbenzylamines employed in the present work, which is part of investigations supported by *Statens*

Almindelige Videnskabsfond (The Danish State Research Foundation) and *Carlsbergfondet* (The Carlsberg Foundation).

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Received December 11, 1956.

A Rapid Method to Determine Sulphur

ROLF OTTOSSON and
OLLE SNELLMAN

*Institute of Biochemistry, University of
Uppsala, Uppsala, Sweden*

In the method of determining sulphur in organic compounds used earlier here and described by Paulson¹, there were certain difficulties inherent in the combustion of the material. To facilitate the measurements and to obtain a better accuracy some modifications have been introduced in the measuring device and the oxidation of the material has been performed according to a modification of a method described by Schöniger². With this method, sulphur determinations have been performed during the last year and the reproducibility has been very good. The method seems to be both rapid and accurate.

Apparatus. For burning the material a 500 ml bottle with a ground stopper is used. A platinum wire is sealed into the stopper. The wire is 10 cm long and has a diameter of 1 mm. A loop is made on the wire according to Fig. 1.

The same kind of measuring apparatus is used as described by Paulson. The milliam-

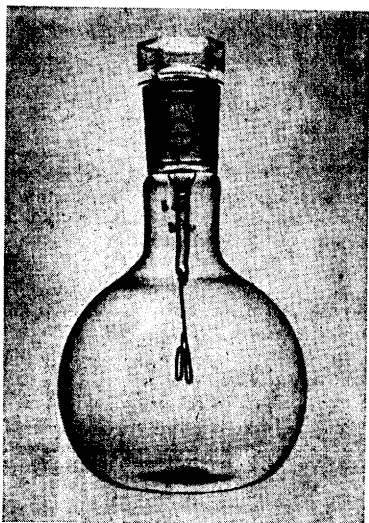


Fig. 1. The burning bottle.

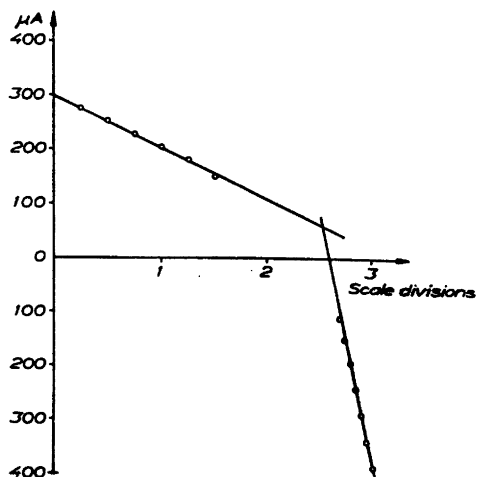


Fig. 2. Example of an analysis curve. The displacement of the micrometer screw is plotted as abscissa and the ammeter reading as ordinate.

meter (Philips mA) is used in such a range that a shift of about 40Ω in the 1000Ω region on the bridge will cause a deflection of the whole scale on the ammeter (0–500 mA).

Method. The sample is burnt according to the method proposed by Schöniger³, but without using the sodium hydroxide. 10 ml distilled water and 2 ml perhydrol are pipetted in the bottle. The last drop of the water in the pipette is used to make a wet zone around the ground stopper. Oxygen is let into the bottle from an oxygen cylinder for about 20 sec. The substance to be tested is wrapped in a filter paper strip and put into the loop in the platinum wire. The end of the strip is lighted and quickly put in the bottle where the substance is burnt in the oxygen. The bottle is left for 30 min. After this time, the ground surfaces are washed with the contents in the bottle, in case the drop on the stopper has absorbed any sulphur dioxide. Of the reaction mixture, 10 ml is transferred to the conductivity cell.

To the 10 ml reaction mixture in the conductivity cell, one drop of 20 % acetic acid and 1 ml of a barium sulphate suspension in distilled water are added. The content of the cell is then vigorously stirred with a rotating glass rod. It is important that the glass rod is not inserted between the platinum electrodes, as

this causes variations in the conductivity and the capacitance of the circuit and hence the needle of the ammeter will not be stable. The apparatus is left for about 10 min for stabilization.

After this time, the apparatus is adjusted to zero deflection and then the resistance is lowered about 40Ω . The barium chloride solution used for the titration is about 0.5 M. It is added in 0.002 ml portions and the readings after every addition are plotted against the total displacement of the micrometer screw.

The points on the steep line are taken after the zero point on the ammeter is passed and the same region of the scale is reached in which the first series of points was taken. The last points are plotted on the negative side of the diagram (Fig. 2). By these symmetric readings the non-linear sensitivity in the system is cancelled.

A calibration curve is given in Fig. 3, where the scission points of the lines are plotted against a known amount of sulphur. Using the same solution we have not detected any shift in the calibration curve over a period of six months. The substance used for calibration was sulfanilamide (Eastman Kodak).

Tests. Cystein hydrochloride (Merck) analytical reagent gave the following values

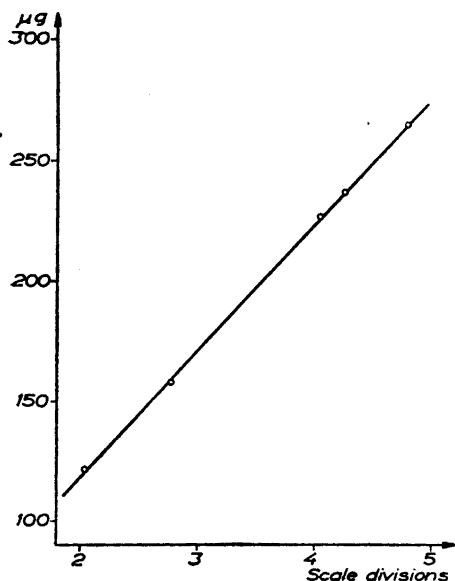


Fig. 3. Calibration curve in the region 100—250 μg . The displacement of the micrometer screw is plotted as abscissa and the sulphur amount as ordinate.

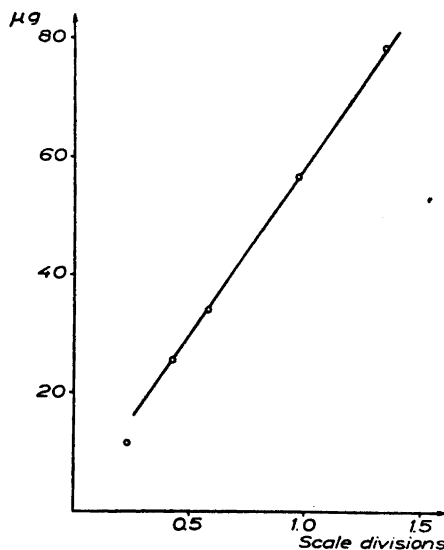


Fig. 4. Calibration curves in the region 20—80 μg . The same abscissa and ordinate as in Fig. 3. The lowest point on the line is not reliable.

Amount	5 per cent
2.57 mg	18.11
2.32	18.20
2.52	18.00
2.04	18.02
Mean	18.08
Calculated	18.32

Methionine (Merck)

Amount	5 per cent
2.08	21.50
1.57	21.80
1.01	21.25
Mean	21.51
Calculated	21.48

The standard error is 0.4 %. In this error is included the error from the weighing of the sample. We used a balance which was graduated in 0.05 mg.

In the region 20—80 μg S, we got the calibration curve Fig. 4 by taking parts of

the absorption fluid from different burnings, diluting to 6 ml in the conductivity cell and adding 1 drop 20 % acetic acid and $\frac{1}{4}$ ml barium sulphate suspension. However, in this case it was very difficult to draw the lines in the diagram as one could get only few points in a narrow interval before the equivalence point was reached.

As the conductimetric titration takes about 5 min and the burning can be done in two bottles alternately, the method is not at all time consuming.

The investigation has been financially supported by a grant from Eli Lilly and Company, Indianapolis, U.S.A.

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Received December 17, 1956.