

585. *Submicro-methods of Organic Analysis. Part XV.**
Determination of Sulphur by the Oxygen-flask Method.

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A simple method is described for the determination of sulphur in microgram samples of organic compounds. The substance is decomposed by combustion in an oxygen-filled flask and the sulphate formed is eventually titrated with barium perchlorate solution in presence of Thorin indicator. Results are as accurate as on the milligram scale. There are few interferences; phosphate can be removed by treatment with magnesium oxide.

THE method described previously¹ for the determination of sulphur in organic compounds is satisfactory, but is lengthy and demands an exacting technique. It has been shown recently that combustion in a closed flask filled with oxygen provides a rapid means of decomposing organic compounds completely on the microgram scale, and the method has been applied to the determination of chlorine.² Hence the possibility of determining sulphur in a similar way was examined.

Determination of sulphur by the oxygen-flask method on the milligram scale presents no difficulties,³ hence no troubles were expected in the submicro decomposition step. The final method of titration, however, provided some problems. The method of completing the determination which was used previously¹ involved precipitation of barium sulphate, filtration, dissolution of the precipitate in EDTA solution, and back-titration with magnesium solution; this was considered inappropriate for use with a simpler method of decomposition. Accordingly, various direct titrations for sulphate were examined; insofar as the sulphate is obtained in an essentially pure solution after the proposed method of decomposition, the choice of finishing method is wider than for other processes of decomposition, *e.g.*, fusion with sodium or the Carius method.

Methods of Titration.—A study of various indicators and titrants for milligram amounts of sulphate showed that only the titrations involving lead ions with dithizone (diphenylthiocarbazone) as indicator in acetic medium,⁴ or barium ions with Thorin [sodium 2-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzenearsonate] as indicator in 80% alcohol⁵ seemed sufficiently promising for microgram adaptation.

The two titrations were therefore tested over the range 4—30 $\mu\text{g.}$ of sulphur. For the titration with a 0.005M-solution of lead nitrate, the aqueous test solution (0.5 ml.) was adjusted with 0.01N-nitric acid until just green to Bromophenol Blue (0.015 ml. of aqueous 0.03% solution), 2.0 ml. of 0.5% w/v acetic acid in acetone and 0.025 ml. of 0.05% w/v dithizone in acetone were added, and the mixture was titrated until the colour matched that of a comparison solution adjusted to the peach colour of the indicator with about 1.7 $\mu\text{l.}$ of the solution of lead nitrate.

The titration with 0.01M-barium perchlorate was carried out as described in the Experimental section. In milligram analysis, an 80% alcoholic solution is generally employed; this concentration did not give an easily visible end-point on the microgram scale but a considerable improvement was effected by increasing the concentration of ethanol to 87—90%. The use of other alcohols instead of ethanol made little difference to the end-points.

The conclusions drawn from these tests can be summarized as follows. The end-points of the two titrations are of similar sharpness; both require the use of comparison

* Part XIV, 1962, 1938.

¹ Belcher, Bhasin, Shah, and West, *J.*, 1958, 4054.

² Belcher, Gouverneur, and Macdonald, *J.*, 1962, 1938.

³ Schöniger, *Mikrochim. Acta*, 1955, 123; Wagner, *ibid.*, 1957, 19.

⁴ Archer, *Analyst*, 1957, 82, 208; White, *Mikrochim. Acta*, 1959, 254; 1960, 282.

⁵ Fritz and Yamamura, *Analyt. Chem.*, 1955, 27, 1461.

solutions for accurate work. The barium method gives a direct proportional relationship between the amounts of titrant used and the sulphate taken over the range examined, whereas the lead method shows a significant deviation (1.5% relative) from proportionality over this range. Another drawback of the lead method is that the dithizone end-point fades in presence of hydrogen peroxide. The latter is needed to convert the sulphur dioxide formed in the combustion to sulphuric acid; tests on the milligram scale have shown that about 80% of the sulphur in the organic compound is converted into sulphur dioxide in the combustion, the remaining 20% being found as sulphur trioxide. However, it is quite difficult to remove hydrogen peroxide without the introduction of ions likely to interfere later and other oxidizing agents would have no advantage in this respect. For these reasons, the barium procedure was preferred for later tests.

On the microgram scale it is generally advisable to standardize solutions against weighed amounts of standard samples, for this allows compensation of weighing errors in actual determinations. However, the barium perchlorate titration is very sensitive to cationic interference,⁵ which proved to be true also on the microgram scale. It was therefore impossible to find a suitable solid standard sulphate; even ammonium ion, which is one of the less severe interferences, caused a positive error of 0.8% relative compared with standardization against 0.005M-sulphuric acid. Attempts to prevent the interference by addition of formaldehyde were unsuccessful, for hexamethylenetetramine must have the same effect as ammonium ion. Accordingly, the solution was standardized against standard 0.005M-sulphuric acid. An indication of the accuracy of the titration over the range 7—40 $\mu\text{g.}$ of sulphur is given by the following: an average figure of 0.01208M was found with an average deviation of 0.000025 and a maximum deviation of 0.00005; this is comparable with standardization on the milligram scale.

Method of Decomposition.—The flask and platinum sample holder were the same as described previously. Polyethylene film as a sample wrapper gave satisfactory blank values of 0.13—0.16 $\mu\text{g.}$ of sulphur (including a fuse). With occasional samples the electrostatic charge of the film made wrapping troublesome and, instead, very small compacted twists (nests) of cotton wool were used; these were reasonably satisfactory but the blank values were *ca.* 0.5 $\mu\text{g.}$ of sulphur, hence the polyethylene film was retained for general purposes. The linen thread which proved excellent as a fuse in the determination of chlorine, contained a metallic ion which formed a coloured complex with Thorin. Cotton thread was therefore used; its combustion characteristics were inferior to those of linen, but blank values were small.

Hydrogen peroxide (30% M.A.R.) was used as the absorbing solution for the products of combustion, in an amount just sufficient to moisten the wall of the flask. When the same volume of peroxide was placed at the bottom of the flask, the recoveries were only 80—90%. The importance of the absorption and rinsing technique is thus emphasized. The amount of water used must be kept to a minimum for the final titration and it is important to pour and shake out all excess of peroxide.

Applications to Organic Compounds.—Replicate analyses on sulphonal showed an average recovery of 100% with a deviation of 1%, thus there is no evidence for systematic errors. The average recovery for all samples not containing phosphorus was 99.8% with a standard deviation of 1.2%. Results on other compounds of known purity are shown in the Table. The accuracy and precision of the method seem to be equivalent to the figures for milligram-scale analysis.

In accordance with previous experience in milligram-scale analysis no interference was found from nitrogen or chlorine in the organic sample. Fluorine did not interfere up to a ratio of fluorine to sulphur of 3 : 1; the microgram method thus shows a greater tolerance for fluorine than the milligram method, despite the increased concentration of ethanol in the solution. This might be due to a proportionally larger area of exposed borosilicate glass, so that fluoroborate complex could be readily formed. There is evidence in

Analysis of organic compounds.

Compound	Sample wt. ($\mu\text{g.}$)	S (%) (calc.)	S (%) (found)	Recovery (%)
Sulphonal (10 results)	47.65—110	28.09	28.09 (27.84—28.43)	100.0
Benzyl disulphide	65.00	26.03	26.15	100.5
	72.25		26.01	99.9
S-Benzylthiouronium chloride	33.07	15.82	15.68	99.1
Phenylthiourea	36.15	21.07	21.10	100.1
	48.31		21.25	100.9
<i>m</i> -CF ₃ ·C ₆ H ₄ ·NEtTos *	77.45	9.33	9.38	100.5
	71.09		9.44	101.2
	51.84		9.20	98.6
(CH ₂ I·CH·OTos) ₂	81.11	9.86	9.63	97.7
	87.39		9.86	100.0
Research sample (non-volatile liquid)	33.97	16.97 †	17.13	100.9
	37.34		16.45	96.9
Sulphonal + Ph ₃ PO ₄	70.09	28.09	27.98	99.6
Benzyl disulphide ‡	92.98	26.03	26.13	100.4
	66.73		25.75	98.9
Benzyl disulphide + Ph ₃ PO ₄	101.42		26.28	101.0
	55.75		26.02	100.0
5-Chloro-4-hydroxy-3-methoxybenzylisothiouraea phosphate	83.58	9.30	9.05	97.3
	71.56		9.24	99.3
	80.78		9.27	99.7

* Tos = *p*-C₆H₄Me·SO₂. † Found by milligram analysis. ‡ Taken through the magnesium oxide separation procedure.

milligram-scale analysis⁶ that boron from glass can form a complex with sufficient fluorine to interfere in the determination of fluorine after decomposition by the oxygen-flask method, hence the same process could prevent the interference of fluorine in this method. However, when a sample containing a 21 : 1 ratio of fluorine to sulphur was analyzed, results were high; addition of boric acid gave inconclusive results owing to large and inconsistent blank values.

Iodine caused high (10% relative) results, which is comparable with the results obtained on the milligram scale. The bulk of the iodine can be removed by evaporation during the initial rinsing procedure; the residual amount does not interfere.

Phosphorus interfered badly in the same way as in milligram-scale analysis. It has been shown⁵ that phosphorus can be removed by appropriate treatment with magnesium carbonate in milligram-scale analysis. In the present microgram-scale analysis, magnesium oxide was tested for this purpose because it is available in a purer form. After the recommended separation (see below) the volume of solution for titration was larger, but this had little effect on the end-point. It proved necessary to add more perchloric acid than the amount required in the usual titration to neutralize the very fine magnesium oxide which passed through the filter. Water must be added to the filtered precipitate to remove adsorbed sulphate, which is not washed out with ethanol. The separation process proved satisfactory; results tended to be high, but were still within the normal tolerated limit of errors.

EXPERIMENTAL

Apparatus.—The microgram balance, the titration apparatus, the flasks for combustion and titration, the oxygen line, and the polyethylene sheet were as previously described.² When the sample contained phosphorus, a filtration apparatus⁷ was required.

Cotton thread was treated in the same way as the linen thread used previously.² Cotton wool was also cleaned in this way.

Reagents.—Glass-distilled water was used throughout.

Barium perchlorate solution. Anhydrous barium perchlorate (3.4 g.) was dissolved in water

⁶ Johnson and Leonard, *Analyst*, 1961, **86**, 101.

⁷ Belcher, Shah, and West, *J.*, 1958, 2998.

(200 ml.) and ethanol (800 ml.). The apparent pH was adjusted to ~ 3.5 with perchloric acid. The solution was standardized against 100- μ l portions of standard 0.005M-sulphuric acid by the titration procedure given below after water had been added to bring the total volume of water to 0.2 ml. After determination of indicator blanks, the titre was calculated.

Ethanol. Spectroscopically pure absolute ethanol was used.

Perchloric acid solution. A 2.5% v/v solution was prepared from perchloric acid of analytical-reagent grade and stored in a glass dropping-bottle with a tip drawn-out to deliver drops of about 0.015 ml.

Thorin indicator. An aqueous 0.1% solution was stored in a dropping-bottle as above. An aqueous 0.002% Methylene Blue screening solution was used, being stored as above.

Hydrogen peroxide. This was the 30% microanalytical reagent grade.

Magnesium oxide. Material of analytical reagent grade was used.

Preparation for Analysis.—This was as described previously.²

Procedure.—A sample containing 10–30 μ g. of sulphur was weighed from a platinum boat on to a Polyethylene square on a dark background. The sample was wrapped,² a double-length twist of cotton thread was inserted as fuse, and the package was fixed in the platinum holder.² The inner wall of the flask was moistened with hydrogen peroxide and the flask shaken to ensure that the amount of peroxide present was just sufficient to wet the wall. The combustion was made in the usual way.²

After 90 min., the rim of the ground joint was wiped with filter paper moistened with ethanol, the stopper raised slightly, and 3 small drops of water (*ca.* 0.04 ml.) were introduced while the raised stopper was rotated. The stopper and the platinum gauze were washed as described previously² with 1.0 ml. of ethanol and 3 small drops of water and allowed to drain for 30 min. Then the flask was opened and rinsing was repeated with another 1.0 ml. of ethanol (no water was used at this point).

The flask was placed on a magnetic stirrer on a white tile covered with filter paper and a washed stirring bar was added. ~ 0.025 ml. of Thorin indicator was added and, if desired, about 0.015 ml. of Methylene Blue screen, then ~ 0.015 ml. of 2.5% perchloric acid solution. The mixture was titrated with 0.01M-barium perchlorate under a "daylight" lamp, 0.2 μ l. increments being used near the end-point, until the colour matched that of a comparison solution. Near the end of the titration, the flask was swirled gently to collect any sulphate that might have crept up the wall.

For the comparison solution, 0.2 ml. of water and 2.0 ml. of ethanol were placed in a small test-tube and indicator and acid added as above. The mixture was titrated to the first permanent pink colour; usually 1.1–1.2 μ l. of 0.01M-barium perchlorate was required. The solution had to be prepared freshly for each series of titrations because the colour tended to fade on storage.

A blank value was obtained by taking an empty sample wrapper through the whole procedure. A normal blank value is 0.5 μ l. of titrant, when Polyethylene is used as the sample wrapper.

In presence of iodine. At the end of the first rinsing procedure, and before draining for 30 min., the solution was evaporated almost to dryness by gentle heating in a stream of oxygen. This serves to remove the bulk of the iodine and prevents its interference. After the evaporation, the wall of the flask was rinsed with 1.0 ml. of ethanol, and the flask was rotated to soak the wall and left for 30 min. The procedure was then as before.

In presence of phosphorus. At the end of the whole rinsing procedure, 0.3–0.5 mg. of magnesium oxide was added and the whole boiled gently with occasional shaking for 5 min., then allowed to cool for 30 min. and filtered through a small pad of filter-paper pulp into a suitable small test-tube. The solution was transferred with a transfer pipette.⁷ The flask was rinsed with 0.5 ml. of ethanol, then suction was stopped, 0.05 ml. of water was added to the filter pad, suction was restarted, the pipette, flask, and filter were rinsed with 0.5 ml. of ethanol, suction was stopped, another 0.05 ml. of water added as above, the suction restarted, washing completed with two 0.5-ml. portions of ethanol.

0.1 ml. of 2.5% perchloric acid and indicator were added and the titration completed as described above.

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