

**815. Submicro-methods for the Analysis of Organic Compounds.
Part V.¹ The Determination of Sulphur.**

By R. BELCHER, R. L. BHASIN, R. A. SHAH, and T. S. WEST.

Sulphur in organic compounds can be determined by decomposing *ca.* 50 μg . samples with fuming nitric acid and anhydrous barium chloride at 275–280°. The precipitated barium sulphate is centrifuged off, washed, and dissolved in an excess of ammoniacal 0.02M-EDTA. The sulphur is determined indirectly by titration of the excess of chelating agent with standard 0.01M-magnesium chloride (screened Solochrome Black T indicator). Average results for any one compound are within 0.20%; no result is likely to exceed by 0.4% the absolute sulphur content.

SEVERAL methods are available for the decomposition of organic compounds in order to determine their sulphur content, *e.g.*, dry oxidation in a stream of oxygen or air, wet oxidation with, *e.g.*, nitric acid, and fusion with an alkali metal or alkali-metal peroxide. Previous experience of absorption of small amounts of material from gas streams led us to consider only the wet oxidation and the fusion methods.

Initially fusion with an alkali-metal was used as this had proved successful in the submicro-determination of bromine and iodine.¹ After fusion as in that work, the sulphide was oxidised by hydrogen peroxide or bromine and sulphate determined by (*a*) passage through an ion-exchange column (hydrogen form) and titration of the eluted sulphuric acid, or (*b*) precipitation as barium sulphate and complexometric titration with disodium ethylenediamine tetra-acetate (EDTA) to determine either the excess of barium chloride² or the precipitated barium salt.³ Both procedures (*a*) and (*b*) were satisfactory when inorganic sulphate was used as the test material. The ion-exchange procedure was unsatisfactory for submicro-determination of sulphur in organic compounds because of the high control values obtained on the reagents. The most successful of the complexometric methods (*b*) was that involving determination of the precipitated barium. However, silicates leached from the glass tube during fusion with metallic sodium interfered. Interference was also observed when the glass tubes, hitherto used in this type of work, were replaced by small nickel bombs. In this instance, traces of nickel leached from the bombs caused replacement of the magnesium used as back-titrant from its EDTA chelate and reacted irreversibly with the hydroxyazo-dye used as indicator. Fusions with sodium peroxide were not practicable because of the impurity of the reagent and difficulties associated with high electrolyte concentration in the resulting solutions. A detailed account of these procedures has been given elsewhere.⁴

The method finally selected was to heat $\sim 50 \mu\text{g}$. of the sulphur compound with $\sim 200 \mu\text{g}$. of anhydrous barium chloride and 50 μl . of fuming nitric acid in a sealed glass tube at 275–280° for 7 hours, evaporate off the nitric acid, dissolve the soluble salts, collect the barium sulphate and dissolve it in a measured excess of EDTA in ammoniacal solution, and titrate the excess of chelating agent.

The results, shown in the Table, refer to substances of known purity (nos. 1–4) and others (nos. 5–9) supplied as unknowns by various workers in this Department. Not all these compounds are of theoretical composition, but in each instance the results obtained by the submicro-method are in close agreement with those obtained by normal organic microanalysis. Sample 10 (thiourea) was selected because of its high sulphur content and gave low results by this method; we attributed this to the presence of insufficient barium chloride, but subsequently found that the excess of EDTA necessary

¹ Part IV, Belcher, Shah, and West, *J.*, 1958, 2998.

² Belcher, Gibbons, and West, *Chem. and Ind.*, 1954, 850.

³ *Idem, ibid.*, p. 127.

⁴ Shah, Ph.D. Thesis, Birmingham, 1957.

to dissolve the increased amount of barium sulphate was the most important factor. When double the previous excess of EDTA was used no further trouble was experienced in this analysis.

Apart from the somewhat long decomposition time, the method is quite rapid. No attempt was made to reduce this time since generally decomposition was allowed to proceed overnight.

Compound	Range of wts. ($\mu\text{g.}$)	Sulphur (%)		Error (%)	No. of Detns.	Range of errors (%)	
		Calc.	Found			Max.	Min.
Sulphonal	49.96—59.53	28.09	28.03	0.06	3	-0.13	+0.04
Benzyl disulphide	50.01—61.08	26.03	26.12	0.09	3	+0.25	-0.05
Phenylthiourea	47.95—57.99	22.86	22.76	0.10	3	-0.19	+0.03
S-Benzylthiuronium chloride ...	52.67—58.34	15.82	15.71	0.11	3	-0.44	± 0.00
1 : 4-Di-iodo-2 : 3-di- <i>o</i> -toluene- sulphonylbutane	50.60—69.88	9.86	9.76	0.10	4	-0.33	-0.11
Na octane-1-sulphonate	47.08—68.69	14.80—14.43 *	14.27	0.16	3	-0.42	+0.06
8-Hydroxy-7-iodoquinoline-5- sulphonic acid	43.33—68.42	9.11, 9.28 *	9.29	0.01	7	-0.12	+0.01
<i>p</i> -Bromo- <i>N</i> - <i>p</i> -methoxyphenyl- benzenesulphonamide	48.60—66.40	9.36, 9.36 *	9.38	0.02	4	+0.29	-0.04
(HO ₂ C·CH ₂ ·S) ₂	47.89—48.33	30.47, 29.78 *	29.65	0.13	4	-0.32	+0.07
Thiourea	47.15—59.98	42.12	42.04	0.08	4	-0.16	+0.04

* Actual analyses by routine micromethod. † Difference from microanalytical result.

In the method we recommend, it is important to use nitric acid of optimum strength (*d* 1.5): incomplete recoveries are obtained with weaker acid. It is also important to observe the recommended procedure for dissolution of the barium sulphate in ammoniacal EDTA. We have used the EDTA procedure on the macro-, the micro-, and the submicro-scale and find that it is relatively much more difficult to dissolve barium sulphate on the submicro-scale. The manner of precipitation of the barium sulphate in the Carius type of procedure may be responsible for this, as it is known that well-aged barium sulphate is considerably more difficult to dissolve than the freshly precipitated variety.

EXPERIMENTAL

Reagents.—(1) Fuming nitric acid (*d* 1.5) of "AnalaR" grade. (2) Anhydrous barium chloride, "AnalaR" dihydrated salt dehydrated at 200° for 6 hr. (3) 1 : 300 Hydrochloric acid, prepared from "AnalaR" reagent. (4) Solochrome Black T indicator, 0.1% ethanolic solution prepared daily. (5) Dimethyl Yellow, 0.05% solution in ethanol. (6) 0.02M-Disodium ethylenediaminetetra-acetate dihydrate, standardised against metallic magnesium. (7) 0.01M-Magnesium chloride, evaluated against standard 0.02M-EDTA. (8) Ammonia, "AnalaR" concentrated reagent. (9) Filter-paper pulp, prepared in the usual way from "Whatman" ashless paper.

Apparatus.—(1) Magnetic stirrer. (2) "Agla" micrometer syringe burettes. (3) 2-ml. hypodermic syringe. (4) Hypodermic needle, 1½", 22 BWG. (5) Transference-pipette. (6) Heating block for Carius digestion, capable of holding 8 tubes at a temperature of 275—280°, electrically heated and controlled by a "Simmerstat." (7) Heating-block (130—135°) for digestion of precipitate with EDTA, similarly heated and controlled. (8) Digestion-tubes prepared from "Pyrex" (1.3 × 7.5 cm.) or "Phoenix Regina" (3" × ½") test-tubes, cleaned as described earlier.⁵ (9) Cylindrical "dural" block bored to hold digestion tubes during cooling. (10) Submicro-filtration device.¹ (11) Semimicro-"Eureka" electric centrifuge. (12) Platinum tetrahedra, to promote smooth boiling. (13) Small glass-encased rotor for use with magnetic stirrer, which must function efficiently in the presence of the platinum tetrahedron.

Procedure.—A 50 $\mu\text{g.}$ sample was weighed on a submicro-balance⁶ and transferred to the

⁵ Belcher, West, and Williams, *J.*, 1957, 4323. On p. 4326, line 6 from the bottom of the page, for potassium iodide read potassium bromide.

⁶ Asbury, Belcher, and West, *Mikrochim. Acta*, 1956, 598.

bottom of a clean dry test-tube by tapping the tweezers holding the inverted platinum weighing-vessel gently against the edge of the tube. The tube itself was gently tapped to prevent the sample's adhering to the walls near the top of the tube. About 200 $\mu\text{g.}$ of anhydrous barium chloride (approximately weighed on the submicro-balance) were then transferred to the bottom of the tube by the same procedure. 50 $\mu\text{l.}$ of nitric acid (d 1.5) were delivered to the tube by means of a syringe burette, and the tubes were sealed near the open end.⁵ Difficulty was sometimes experienced in sealing the tubes owing to the vapour pressure of the acid, but the procedure was simplified if the test-tube was drawn out near the end, cooled, and then sealed.

The sealed tubes were placed in the cold heating-block with just the tip protruding and the temperature was raised and kept at 275—280° overnight (or for at least 7 hr.). The heating-block was switched off and the tubes were removed when nearly cool. They were then centrifuged for 5 min. and the pressure in the tubes was released by heating the tip of each tube in a flame. The tubes were opened near the top in the usual way.⁵

The walls of each tube were washed down with 1 ml. of distilled water from a 2 ml. hypodermic syringe. The tubes were centrifuged once more for 1 min. and the contents evaporated to dryness in the heating-block, now adjusted to 100—110° by means of the Simmerstat control. 1 ml. of 1 : 300 hydrochloric acid was added to each tube and the temperature was kept at 90—100° for 30 min. The tubes were then removed from the heating-block and set aside for *ca.* 2 hr. after which they were centrifuged for a further 5 min. The supernatant liquid in each tube was next removed by means of a transference-pipette, care being taken to remove as little barium sulphate as possible, and filtered on the submicro-filtration apparatus through paper-pulp, under gentle suction. 1 ml. of 1 : 300 hydrochloric acid was again added to the tube which was then centrifuged for a further 5 min. The transference and filtration were repeated as before. The whole process was repeated with two 0.5 ml. lots of distilled water. Finally the pulp-pad was transferred back to the tube by means of a hypodermic needle. Washings from (1) the funnel, (2) the inside and outside of the transference pipette, and (3) the tip of the hypodermic needle (not more than 1.5 ml. in all) were then collected in the tube. Finally, 100 $\mu\text{l.}$ of 0.02M-EDTA were added from a syringe burette, two drops of concentrated "AnalaR" ammonia, and a platinum tetrahedron. The mixtures were then brought to the b. p. during 4—5 min. by placing the tubes in the heating-block at 130—135°; boiling was maintained for a further 5 min. The tubes were removed and cooled, and the contents treated with a further drop of ammonia, brought to the b. p. once more (4—5 min.), and boiled for a further 5 min. The tubes were finally taken out of the heating-block, cooled, and centrifuged for 1 min. A small glass-encased iron rotor was added to each tube and the excess of EDTA was titrated with standard magnesium chloride from a syringe burette after addition of one drop each of Solochrome Black T, Dimethyl Yellow, and concentrated ammonia. The colour change at the end-point was from green to *just* red.

A control analysis carried out on the reagents was usually negligible.

For compounds of high sulphur content, *e.g.*, thiourea (S, 42.1%), a larger amount of anhydrous barium chloride should be used (250—300 $\mu\text{g.}$), and 200 $\mu\text{l.}$ of 0.02M-EDTA for dissolution of the larger amount of barium sulphate involved.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
BIRMINGHAM, 15.

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