688. *Submicro-methods for the Analysis of Organic Compounds.*
Part XVIII.* The Determination of Bromine and Iodine.

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Bromine or iodine in 50 μg. samples of organic materials is determined by combustion of the sample in an oxygen-filled flask. After suitable oxidation processes, the halate is titrated by indirect iodimetry. The methods are simple and as accurate as on the milligram scale.

IT has been shown [1,2] that the conventional oxygen-flask method for the decomposition of organic materials can be modified to allow simple and relatively rapid determinations of chlorine and sulphur in organic samples weighing only 30—80 μg. The method was therefore extended to determinations of iodine or bromine in similarly small samples, so as to supersede the previously described method [3] based on fusion with alkali metal in a sealed tube. As in the earlier work [3] modifications of the amplification methods involving hypochlorite [4] and bromine [5] oxidations were applied to determine the halides formed by the combustion. A few results indicated that the mercurimetric method described earlier for chlorine [1] should be applicable to determination of bromine, but the conversion factor is poor, and would be prohibitively so for the determination of iodine. In any case, the amplification methods are preferable because there is no interference from other halogens.

Determination of Bromine.—In the milligram-scale oxygen-flask procedure, the products of combustion are generally absorbed in the buffered hypochlorite solution used for the oxidation of bromide to bromate.[6] This was also found satisfactory on the microgram scale; buffered hypochlorite is preferable to other absorbents, because the electrolyte content of the final solution can be kept to a minimum with consequent benefit to end-point detection. In earlier determinations involving the oxygen-flask,[1,2] rinsing of the flask walls after combustion wss done most efficiently with ethanol. Ethanol or another organic liquid could not be used in the present application, because it would consume hypochlorite or decrease the sensitivity of the final starch–iodine end-point. Water was therefore used for rinsing, its lower efficiency being compensated for by rolling the absorbent solution over the flask wall and by increasing the drainage periods. It must be stressed that the rinsing and drainage technique recommended under " Procedure " is essential for accurate results; if the rinsing, etc., is shortened, results will generally be low by 1—2% absolute.

The correct pH value and temperature for the oxidation are of great importance. With the diluted commercial sodium hypochlorite solution used, it was advisable to ascertain the amount of phosphate buffer needed to obtain a pH of *ca.* 6·2 by micro-tests with a pH meter, and then to adjust the amounts proportionately for the submicro-determinations; such adjustment was, of course, needed only for each fresh batch of concentrated sodium hypochlorite solution. To ensure complete oxidation of bromide by hypochlorite, the solution must be heated in a heating block to 98°, the temperature and time of heating being quite critical. Another critical point is the decomposition of excess of hypochlorite with sodium formate; heating followed by gradual cooling was necessary. These points by no means apply only to the present submicro-procedure, but are of importance on all scales of working.

Representative results for a series of organic compounds are shown in Table 1. For 14 replicate analyses of micro-analytical standard grade bromobenzoic acid, the average

* Part XVII, *J.*, 1963, 5720.

[1] Belcher, Gouverneur, and Macdonald, *J.*, 1962, 1938.
[2] Belcher, Campbell, Gouverneur, and Macdonald, *J.*, 1962, 3033.
[3] Belcher, Shah, and West, *J.*, 1958, 2998.
[4] Kolthoff and Yutzy, *Ind. Eng. Chem., Analyt.*, 1937, **9**, 75.
[5] Leipert, *Mikrochemie*, 1929, 266.
[6] Schöniger, *Mikrochim. Acta*, 1955, 123; 1956, 869.

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TABLE 1.

Analysis of bromine-containing organic compounds.

Compound	Sample wt. (μg.)	Br (%), required	Br (%), found	Recovery (%)
Bromobenzoic acid (14 results)	35 to 87	39·75	39·68 (39·16—40·29)	99·76
p-Nitrobenzyl bromide	54·15, 43·59	36·99	36·64, 37·05	99·05, 100·16
p-Bromoacetanilide	55·87, 31·58	37·33	37·01, 37·30	99·14, 99·92
p-Bromophenacyl bromide	56·73, 48·71	57·50	57·34, 57·25	99·72, 99·56
6-Bromo-1,3 : 2,4-diethylidenesorbitol	47·46, 48·28	26·90	27·31, 26·78	101·52, 99·55
2,4,6-Tribromoaniline....................	28·25, 35·95	72·68	72·67, 72·55	99·99, 99·82
5-Bromovanillic acid	57·41, 59·15	32·40	32·31, 32·32	99·72, 99·75

recovery was 99·76%, and the average absolute error was $\pm 0.28\%$, with a maximum absolute error of $\pm 0.6\%$. Over the entire series the average recovery was 99·84%, with an average absolute error of $\pm 0.2\%$. These figures are based on standardisation of the thiosulphate solution against primary standard potassium bi-iodate. Calculation of a series of results based on standardisation against potassium bromide through hypochlorite oxidation showed an average recovery of 100·2%; the bi-iodate method was considered the more reliable. The slightly negative error in the total recovery of organic bromine then obtained indicates that the hypochlorite oxidation was not 100% quantitative even under the optimum conditions, for with sulphur [2] and iodine (see below), the overall average recoveries were almost exactly 100%, which shows that the decomposition and absorption techniques are unlikely to be faulty. However, no matter which factor is used, the results are generally within the permissible limits of error, and on the basis of accuracy and freedom from interference, the hypochlorite oxidation method must be considered the most suitable for bromide, particularly on the submicro-scale.

Determination of Iodine.—Certain difficulties were encountered in preliminary tests when sodium hydroxide solution was used as absorbent and the Leipert bromine oxidation method [3,5] was applied. (Bromine-containing solutions could not be used as the absorbent because of variable side-reactions.) Modifications in the oxidation method [3] to make the conditions less critical, and in the absorption and rinsing technique to avoid adsorption of iodine leading to negative results, overcame these difficulties. Yet again, it proved essential to rinse the flask wall and drain it correctly in order to recover the last traces of the required ion in the solution to be titrated. It was shown that there was no reaction of formate with iodate under the conditions used, and the initial low results were almost definitely due to adsorption of iodine on the glass encouraged by the alkaline absorbent. As for the determination of bromine, no alcohol could be present in the solution before oxidation.

Apart from its simplicity, the oxygen-flask procedure for iodine has the advantage over the alkali metal-fusion procedure that organic nitrogen does not interfere. In the latter method, cyanide is formed, whereas in the flask method, oxides of nitrogen formed in the decomposition are subsequently converted into nitrate during the oxidation.

Representative results for a series of organic compounds are shown in Table 2. The average recovery for 12 replicate analyses of microanalytical standard-grade iodobenzoic acid was 100·02%, and the average absolute error was $\pm 0.18\%$, with a maximum absolute error of $\pm 0.5\%$. The average recovery for all the compounds tested was 100·06%, which indicates that there is no significant bias in the method. Standardisation of the thiosulphate solution against potassium bi-iodate and against pure potassium iodide through bromine oxidation gave no significant difference in results (*cf.* determination of bromine).

The hypochlorite-oxidation procedure for bromine also gave very satisfactory results for iodine; thus it should be possible to determine iodine and bromine in the same compound by burning two samples and determining the total iodine and bromine by hypochlorite oxidation, and the iodine alone by bromine oxidation; such a procedure is quite

TABLE 2.

Analysis of iodine-containing compounds.

Compound	Sample wt. (μg.)	I (%), required	I (%), found	Recovery (%)
Iodobenzoic acid (12 results)	33—65	51·17	51·19 (50·9—51·65)	100·03
2-Hydroxy-3,5-di-iodobenzoic acid ...	31·48, 31·48	65·09	65·14, 65·42	100·08, 100·51
Hexamineallyl iodide	37·48, 33·20	41·21	41·33, 41·40	100·29, 100·46
5-Chloro-8-hydroxy-7-iodoquinoline ...	51·45, 42·53	41·54	41·55, 41·04	100·02, 98·80
1,4-Di-iodobutane-2,3-diol	36·27, 57·02	74·23	74·58, 75·06	100·47, 101·12
trans-2-Hydroxycyclohexyltrimethyl-ammonium iodide	44·33, 46·13	44·50	44·10, 44·74	99·10, 100·50
p-Iodoacetanilide.........................	31·49, 33·77	48·61	48·50, 48·59	99·77, 99·96

satisfactory on the micro-scale,[7] though aliquot portions are generally taken instead of separate samples.   Various attempts were made to determine bromate and iodate on the microgram scale by successive iodometric titrations on the same solution,[8] but no wholly satisfactory procedure could be developed.

EXPERIMENTAL

Apparatus.—The microgram balance, titration apparatus, flasks for combustion and titration, oxygen line, polythene sheet, and linen thread were as described previously.[1]   The electrically heated Dural block for heating the solutions during hypochlorite oxidation has been described previously.[3]

Reagents.—Water distilled in glass apparatus was used throughout.   All reagents, except hypochlorite, were of AnalaR grade.

Sodium thiosulphate.   This was *ca.* 0·01N, containing 100 mg. of sodium carbonate per litre of boiled-out distilled water.   The solution was standardised against pure potassium bi-iodate as follows: 60—80 μg. of standard were weighed into a dry flask, which was then rinsed down with 2 ml. of distilled water; acid and iodide solutions were added as described in the final step of the procedures given below and the solution was titrated with thiosulphate.

Potassium iodide.   A freshly prepared 10% solution in water was stored in a capillary dropping bottle of brown glass.

Reagents for the Determination of Bromine.—*Sodium hypochlorite.*   An approximately 1N solution was prepared every 2—3 weeks by 1 : 3 dilution of commercial (Imperial Chemical Industries Limited) " bromine-free " reagent, and stored in a dark bottle.

Potassium dihydrogen phosphate.   A 10% solution was used.

Sodium formate.   9 g. of sodium hydroxide was dissolved in 20 ml. of water, and 9·5 ml. of 90% formic acid was carefully added dropwise.   The solution was stored in a polythene dropping bottle, and was stable for *ca.* 2 weeks.

Ammonium molybdate (3% w/v) and 12 N-*sulphuric acid.*   These were stored in capillary dropping bottles.

Reagents for the Determination of Iodine.—Bromine water (saturated aqueous solution), formic acid (90%), Methyl Red (an aqueous 0·05% solution of the sodium salt), 2N-sodium hydroxide, and 2N-sulphuric acid were all stored in capillary dropping bottles.   The bromine water was normally kept in a fume cupboard to avoid high blanks in the determinations.

Preparation of Flasks for Analysis.—As described previously.[1]

Procedure.—*Decomposition.*   A sample of 30—80 μg. was weighed on to a polythene square and attached, with a linen fuse, in the platinum sample holder.[1]   The absorbent solution was introduced into the bottom compartment of the flask (see below).   The flask was then filled with oxygen, and the combustion was done as described previously.[1]

After the combustion, the flask was rotated for 1 min. to spread the absorbent over the lower third of the bulb of the flask.   It was then left in a vertical position, protected from the atmosphere, for 30 min., rotated for 3 min. as before and again left for 30 min.   The rim

[7] Belcher, Nutten, and Macdonald, *Mikrochim. Acta*, 1954, 104.
[8] Gawargious, Ph.D. Thesis, Birmingham, 1963.

of the ground joint was wiped with moist filter paper, and the sample carrier and the flask wall were rinsed with 1·5 ml. of water by the previous technique,[1] except that no ethanol was used and the solution was not rolled over the flask wall; especial care was taken to ensure that each portion of water covered as much of the surface to be rinsed as possible. The stopper was then replaced, and the flask wall was allowed to drain for 30 min. The rinsing was then repeated with 0·5 ml. of water, and a further 30 min. drainage time was allowed.

Determination of bromine. The absorbent was 0·3 ml. of the hypochlorite solution delivered from a 1-ml. measuring pipette, and the amount of phosphate solution (*ca.* 0·3 ml.) required to ensure a pH of 6—6·5 for the oxidation. [To estimate this amount, phosphate solution (x ml.) was added to 10 ml. of the hypochlorite solution and 70 ml. of water until a pH of 6·2 was obtained on a pH meter; the volume of phosphate required for the absorbent was then $x \times 0·03$ ml.] These solutions were mixed well, and the flask was then rotated so as to spread them over the flask wall, except for the ground joint, before the combustion.

After the detailed rinsing and draining, a magnetic stirring bar was introduced and the solution was well mixed before being placed in the heating block for 15 min. The latter was previously adjusted to a temperature of $98 \pm 1°$ measured in the flask wells ($120 \pm 1°$ measured in a small thermometer hole). Near the end of this time, the flask just above the liquid level was rinsed with 0·1 ml. of water. Then several micro drops (*ca.* 0·15 ml.) of sodium formate solution were added, with the flask still in the block. The solution was then stirred for *ca.* 30 seconds and replaced in the block for 1 min. It was then covered loosely and allowed to cool very gradually (with the lower portion of the flask inside, *e.g.*, a cardboard case). When cold, the portion just above the liquid level was again rinsed with 0·1 ml. of water.

The flask was then stirred and 1 micro drop (*ca.* 0·015 ml.) of the molybdate solution, 8—10 micro drops (*ca.* 0·15 ml.) of 12N-sulphuric acid and 10 micro drops (*ca.* 0·15 ml.) of the iodide solution were added. After 1 min. the mixture was titrated with the thiosulphate solution from an Agla burette, a little Thyodene indicator being added near the end-point, and the final increments of titrant being 0·1 μl. A white background and a comparison solution of water were preferable. Near the end-point, the flask was swirled to include any iodine accumulated above the liquid level.

Determination of iodine. The absorbent was 4 micro drops (*ca.* 0·1 ml.) of 2N-sodium hydroxide, which was placed in the bottom compartment of the flask. The absorbent was not spread over the flask wall, which was moistened only with water (0·1 ml.).

After the detailed combustion and rinsing, a magnetic stirring bar was introduced, and the solution was well mixed. One micro drop (0·02 ml.) of aqueous Methyl Red was added, and the solution was neutralised to an orange colour with 2N-sulphuric acid added from an Agla burette. This burette was removed after its tip had been rinsed with 0·1 ml. of water. Several drops (0·15 ml.) of the bromine water were introduced and the solution was stirred for 5 min. Then several drops (0·12 ml.) of formic acid were added and the solution was stirred for 10 minutes with slight suction over the flask mouth during the last few minutes to remove residual bromine vapours.

Then 2 micro drops (0·05 ml.) of 2N-sulphuric acid, and 3 drops (0·15 ml.) of the iodide solution were added, and after 1 min. the solution was titrated with 0·01N-thiosulphate as described for bromine.

Blank determinations. Blanks were determined by taking an empty sample wrapper through the entire procedure. The usual blank values were 3—4 μl. of 0·01N-thiosulphate for bromine, and 2—3 μl. for iodine.

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