364. *Submicro-methods of Organic Analysis. Part XIV.* The Determination of Chlorine.*

By R. BELCHER, P. GOUVERNEUR, and A. M. G. MACDONALD.

The determination of chlorine in organic compounds on the submicro-scale has been accomplished by combustion of the sample in an oxygen-filled flask, absorption in water, and eventual mercurimetric titration with diphenylcarbazone as indicator. The method is simple and almost as accurate as micro-methods.

THE main problem involved in the determination of chlorine on the submicro-scale was to find a suitable end-determination. None of the conventional titration methods (argentimetric, mercurimetric, etc.) was sufficiently sensitive, hence some lesser known methods were examined.

It is not possible to amplify chloride by oxidizing it to the halate (as with bromide or iodide) but indirect amplification methods are available [1] in which the chloride solution is treated with silver, mercury(I), or mercury(II) iodate, and soluble iodate equivalent to the original amount of chloride is released. These methods and Berg's iodometric method [2] were examined. The mercury(I) iodate method [3] was the best. The sample was decomposed by fusion with sodium, and the chloride was determined by this procedure. A large range of compounds was examined and satisfactory results were obtained,[4] but the method was lengthy and tedious; several hours were required for complete reaction with mercury(I) iodate and an exacting and carefully controlled filtration technique was needed. The problem was therefore re-examined and different methods of decomposition and titration were studied.

Method of Decomposition.—Decomposition of organic material by combustion in a closed flask filled with oxygen was suggested by Hempel [5] in 1892, but received little attention until 1954,[6] since when the method has been widely adopted for micro- and semimicro-analysis.[7,8] This rapid and simple technique has the advantages of a static as opposed to a dynamic system, and allows eventual titration of the products of combustion in an essentially pure solution; hence it seemed ideally suited to submicro-work.

Preliminary tests were made with electrical-spark ignition of the sample placed in a platinum foil cup (thickness 0·04 mm.; diam. 5 mm.) suspended by platinum wire from the ground-glass stopper of a 1 cm. × 8 cm. test-tube filled with oxygen. Introduction of impurities from wrapping materials and fuses was thus avoided but a spark sufficiently

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* Part XIII, *J.*, 1961, 480.

[1] Belcher and Goulden, *Mikrochim. Acta*, 1953, 290.
[2] Berg, *Z. analyt. Chem.*, 1926, **69**, 1.
[3] Avaliani, *Zavodskaya Lab.*, 1946, **12**, 179.
[4] Bhasin, Ph.D. Thesis, University of Birmingham, 1959.
[5] Hempel, *Z. angew. Chem.*, 1892, **13**, 393.
[6] Mikl and Pech, *Chem. Listy*, 1952, **46**, 382; 1953, **47**, 904.
[7] Schöniger, *Mikrochim. Acta*, 1955, 123; 1956, 869.
[8] Macdonald, *Analyst*, 1961, **86**, 3.

strong to ignite most samples also perforated the foil; the use of thicker foil, or materials other than platinum, caused incomplete combustion.

A flask (Figure) was then designed to allow ignition with a sample wrapper and fuse as on the micro-scale. The bulb of the vessel was of appropriate size to contain enough oxygen for complete ignition of up to 5 mg. of organic material (sample and wrapper) and the bottom compartment formed a suitable container for the liquid eventually to be titrated; the total capacity of the flask was about 25 ml. Several materials were examined for wrapping the sample and for the fuse; the ubiquity of chloride presented a particular difficulty. Wrappers of filter paper or cigarette paper gave high and erratic blank values, but very thin polythene sheet proved highly satisfactory as to blank values and combustion characteristics. The best fuse material was pre-treated linen thread. The average total blank value from the sheet and thread was 0·09 μg. of chloride; a similar size of paper fuse alone gave a blank of about 0·3 μg. of chloride.

Method of Titration.—A mercurimetric titration of chloride has recently been described [9] in which the clarity of the end-point with diphenylcarbazone indicator is very greatly enhanced by the use of a medium containing about 80% ethanol. Experience gained on the micro-scale indicated that the method could be adapted to submicro-work, for the end-point is very much sharper than that of any other argentometric or mercurimetric titration.

The titration was tested for 0—30 μg. of chloride (as sodium chloride) in 2 ml. of solution containing 80% ethanol. Standardisation of an approximately 0·02N-mercury(II) nitrate against measured volumes of sodium chloride solution in this range gave an average figure of 0·01726N (average deviation 0·000036; maximum deviation 0·00007). The deviations showed no significant relation to the amounts of titrant required, but as was expected, the normality found differed slightly from that found in micro-titrations of chloride. There was no significant difference between the figures obtained from weighed amounts of solid sodium chloride, and from measured volumes of chloride solution; this indicated that both the balance and the Agla burettes used were of unexpectedly high accuracy. No improvement in precision was found with 0·01N-mercuric nitrate solutions.

The end-points were sharpest when Bromophenol Blue was used as a screen for diphenylcarbazone; the former indicator also served in the preliminary adjustment of the solution to pH 3·5 with 0·05N-nitric acid. Indicator blanks were held within acceptable limits by measuring the drops added from roughly calibrated capillary droppers. The ethanolic content of the solution could be varied from 70 to 87% without the end-point or the normality factor being affected. However, it was found that even spectroscopically pure ethanol contained some chloride (up to 0·3 μg./ml.), and it was advisable to add the same amount of ethanol in each titration. 2-Propanol showed a much larger chloride content than ethanol and its use in place of ethanol was not further examined.

Applications to Organic Compounds.—When this titration was applied to the liquid absorbent (water and hydrogen peroxide) after combustion of *p*-chlorobenzoic acid, recoveries were about 50% after storage for 15 minutes and 95% after 70 minutes. The 5% loss was traced to adsorption of chloride on the wall of the flask. The scrupulous cleaning and rinsing technique (see later) overcame this difficulty. Pretreatment of the flasks with silicone repellant was less successful. It was important to keep the volume of absorbent as low as possible in order to maintain a final volume of solution, after rinsing the wall and gauze with ethanol, not exceeding 2 ml. of 80% ethanol; ethanol could not, of course, be present in the absorbent. Mere wetting of the wall of the flask with water sufficed for the absorbent when a storage time of 90 minutes was used. The normal practice in micro- and macro-analysis of adding hydrogen peroxide to the absorbent solution for the determination of chlorine was unnecessary; tests showed no difference in the recoveries of chlorine whether or not peroxide was added. This was true even for compounds which contained no hydrogen, when chlorine rather than hydrogen chloride

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[9] Cheng, *Microchem. J.*, 1959, **3**, 537.

could be expected to be formed. Whatever the course of the reaction a large amount of hydrogen would be available from the sample wrapper. Accordingly, hydrogen peroxide was omitted from later tests because of the advisability of keeping the number of reagents to a minimum on this scale of operation.

A wide variety of compounds was analysed by the suggested method; successive results are given in the Table. The average recovery of chlorine was 99·7% (standard deviation 1·56%).

TABLE 1.

Compound	% Cl (theory)	Sample weight (μg.)	% Cl (found)	Recovery (%)
p-Chlorobenzoic acid (8 results)	22·65	36·45—79·25	22·51 (22·25—22·76	99·4
1-Chloro-2,4-dinitrobenzene	17·50	40·68	17·76	101·4
		39·74	17·63	100·8
S-Benzylthiouronium chloride	17·49	52·69	17·36	99·3
		37·49	17·87	102·2
		73·58	17·40	99·6
p-Chlorotrifluoroacetanilide	15·85	44·52	16·20	102·2
		48·37	15·90	100·3
Bisfluorophenyltrichloroethane	32·87	47·25	31·90	97·1
		97·74	32·81	99·8
Monochloroperfluorododeca-*x*,*y*-diene	6·14	51·83	6·14	100·0
5-Chloro-4-hydroxy-3-methoxybenzylisothiouronium phosphate	10·29	75·40	9·85	96·0
		59·47	10·27	99·9
Hexachlorobenzene	74·70	38·52	73·90	98·9
		26·47	74·27 *	99·4
		36·41	73·72	98·7
		31·66	75·45	101·0
1-Chloronaphthalene (impure research sample)	20·40 †	56·41	20·70	101·4
		76·64	20·10	98·6

* Using hydrogen peroxide as the absorbent instead of water (walls wetted with 30% H_2O_2 solution).

† Found by milligram analysis.

An involatile liquid sample was analysed successfully by dipping the end of the linen thread into a weighed portion of sample in the platinum boat, and then reweighing the boat. The tip of the thread was wrapped in the polythene sheet and the analysis was done in the usual way. This method seems of general applicability for involatile samples, but further development is necessary for weighing volatile liquids on this scale.

EXPERIMENTAL

Apparatus.—*Microgram balance.* An Oertling QO1 quartz-fibre balance was used, with normal accessories, such as submicro-platinum boat, platinum spatula, platinum-tipped forceps, etc.

Flasks. These were as shown in the Figure; the capacity was approximately 25 ml. The stopper was a BS B14 airleak into which a platinum wire (0·3 mm. diam.; 50 mm. long) was sealed. Platinum gauze (80 mesh; 13 × 3·5 mm.) was attached to the wire by winding the wire round the gauze several times; spot-welding must be avoided because it leads to negative blanks. The position of the gauze was adjusted to the exact centre of the bulb portion of the flask.

Titration Apparatus.—An Agla syringe burette was used; the inner diameter of the capillary tip must not exceed 0·2 mm., otherwise the aqueous titrant diffuses into the 80% ethanolic titration medium.

Polythene sheet. Even the thinnest commercially available sheet was too thick. Suitable sheet was made from polythene tubing (previously washed with water and ethanol) by blowing out a warmed portion to a thickness of approximately 0·01 mm. This was cut into 15-mm. squares; each piece should then weigh about 2 mg. Pieces were stored between filter paper.

Linen thread. Linen cord thread was wound around a microscope slide, soaked overnight in ethanol–water (1 : 1), washed thoroughly with this mixture, and dried at 110° for 3 hr. It was stored in a closed bottle and standard lengths were cut as required.

Reagents.—Glass-distilled water was used throughout.

Mercuric nitrate solution. 3 g. of mercuric nitrate were dissolved in 500 ml. of 0·01N-nitric acid, and set aside for at least 48 hr., then any precipitate was filtered off and the filtrate diluted to 1 l. The solution was standardised against primary standard sodium chloride as follows:

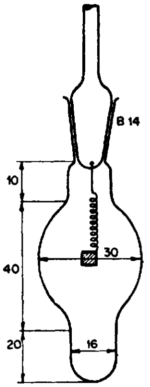
Portions (20—40 µg.) of sodium chloride were weighed from the platinum boat into test-tubes (60 × 15 mm.). The wall of each tube was washed carefully with 0·1 ml. of water from a hypodermic syringe, and 2·0 ml. of ethanol, also from a hypodermic syringe. Bromophenol Blue, nitric acid, etc., were then added and the solution was titrated as described below for the actual determination.

Bromophenol Blue. An aqueous 0·03% solution was stored in a glass dropping bottle with a drawn-out tip to deliver a drop of about 0·015 ml.

Diphenylcarbazone. Ethanolic 0·5% solution was stored as described above in a dropping bottle.

Ethanol. " Spectroscopically pure absolute " ethanol was used.

Nitric acid. 0·05N-Solution was prepared from " Microanalytical Reagent Grade " nitric acid and was stored as described above in a dropping bottle.



Oxygen flask for microgram-scale application.
(Dimension in mm.)

Oxygen. A tube containing soda–asbestos was inserted in the line from the oxygen cylinder. Washed rubber tubing was used, attached to a glass outlet and protected from atmospheric contamination when not in use, for introduction of oxygen into the flasks.

Preparation for Analysis.—The flasks were filled with concentrated (40%) hydrofluoric acid–Teepol mixture (1 : 20), left for 5—10 min. and then emptied and washed abundantly with hot tap water. The flasks were then steamed for at least 10 min. in an apparatus of the type suggested by the Niederls.[10] The stopper was rinsed with distilled water and ethanol, and the unfolded gauze and wire were strongly ignited in a Bunsen flame. The flask was stoppered immediately after taking it from the steaming apparatus and stored in an empty desiccator. This treatment was repeated between analyses.

Procedure.—The optimum amount of sample contained 20—25 µg. of chlorine. Samples of 30—80 µg. were weighed (to the nearest 0·01 µg.) from a platinum boat on to a polythene square on a dark background. The edges of the sheet were folded over the sample, by using two pairs of platinum-tipped forceps. This small bag was rolled around the end of a standard length of linen thread, and the wrapped sample then clamped firmly in the platinum gauze with the aid of platinum-tipped forceps with the fuse projecting in a line with the platinum suspension wire.

The flask was shaken out several times, to ensure that the amount of water present was just sufficient to wet the wall, and then filled with purified oxygen by introducing a rapid stream near the lower compartment for about 30 sec. The position of the gauze was adjusted if necessary, so that it was in the centre of the bulb-shaped portion during ignition. The cone of the stopper was moistened with a small drop of water, the linen fuse lit at a small flame (from chlorine-free alcohol), and the cone inserted quickly into the flask, which was inverted meanwhile. After the combustion, the whole apparatus was placed upright in an empty desiccator for 90 min.

The rim of the ground joint was wiped with filter paper moistened with ethanol, the stopper

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[10] Niederl and Niederl, " Micromethods of Quantitative Organic Analysis," J. Wiley and Sons, Inc., New York, 1942, p. 53.

lifted a few mm., and 0·1 ml. of distilled water introduced from a hypodermic syringe. The partially released stopper was rotated several times, so that no water was lost. 1·0 ml. of ethanol was then introduced from a hypodermic syringe in the following way. The stopper was raised and rinsed with 0·5 ml. of ethanol from a hypodermic syringe; the platinum gauze was rinsed with 3 small drops of water from a syringe, the gauze being drained between drops. The socket was rinsed with 0·5 ml. of ethanol and then inserted and the flask rotated for 3 min. so that the wall was continuously wetted without the stopper and socket being touched. The flask was allowed to drain for 45 min., and then opened and the washing repeated with 1·0 ml. of ethanol and 3 small drops of water.

The flask was placed on a magnetic stirrer on a white tile covered with filter paper, and a washed stirrer added, followed by about 0·015 ml. of Bromophenol Blue solution, about 0·015 ml. of 0·5N-nitric acid (so that the colour of the solution was pure yellow), and about 0·025 ml. of diphenylcarbazone solution. With different batches of indicators, it was advisable to check which volume gave the best end-point. The tip of the Agla burette containing 0·02N-mercuric nitrate solution was introduced and the solution titrated to the first permanent reddish colour, 0·05 μl. increments being used near the end-point. Near the end of the titration, the flask was swirled gently to collect any chloride that might have crept above the liquid level.

A blank value was determined by taking an empty sample wrapper through the whole procedure. A normal blank value was 1·2 μl. of 0·02N-mercuric nitrate solution. Higher values point to contamination of reagents or apparatus.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON, BIRMINGHAM 15.

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