400. *Identification of the Halogen in Organic Halogen Compounds.*

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A microchemical procedure is described for detecting chloride, bromide, and iodide, separately or in admixture. The procedure uses common reagents, and may be applied either to the solution obtained after the microfusion test for elements in organic compounds, or to ordinary inorganic mixtures.

IN a recent paper (*Analyst*, 1938, **63**, 332) one of us (C. L. W.) described micro-tests for nitrogen, sulphur, and halogen in organic compounds. While studying methods for the final identification of the halogen, it was noted that silver chloride and bromide crystallised in different forms from concentrated ammonia, although it is often stated that the halides can neither be distinguished microscopically nor separated through their different solubilities in, say, ammonia (see, *e.g.*, Chamot and Mason, " Handbook of Chemical Microscopy," 1931, II, 341; Groth, " Chemische Kristallographie," 1906, I, 200; Mellor, " Inorganic and Theoretical Chemistry," 1923, III, 393, 419; Higson, *Phot. J.*, 1920, 143; Krohn, *ibid.*, 1918, 193). The characteristic forms of the halides have been noted by Böttger (*Mikrochem.*, 1936, 47) and Kramer (" Mikroanalytische Nachweise anorganischer Ionen," 1937, 2, 26), who, however, do not describe satisfactory methods for their separation in mixtures.

Methods of separation which are effective on the macro-scale fail on the micro-scale, and vague descriptions (such as denoting the strength of ammonia solutions merely by " weak " or " strong ") enhance the difficulty of their application in such cases.

The method here described, in which precisely defined conditions are used, makes it possible to distinguish under the microscope between chloride, bromide, and iodide, and also to detect any one of them in the presence of fairly large quantities of either or both of the others.

The method is based on the following experimental facts : (i) The crystal forms of silver chloride and bromide, when crystallised separately from concentrated ammonia, are entirely different, the predominant forms for the chloride being octahedra, cubes, and squares, and those for the bromide being triangular and hexagonal plates. This is invariably the case under the experimental conditions described. (ii) Although these crystal forms do not always appear in the crystals obtained from a mixture of chloride and bromide, the two salts can be separated sufficiently to ensure that characteristic crystals of each will be formed. (iii) Silver iodide is easily separated from the other two silver halides, and gives a characteristic crystalline derivative when dissolved in pyridine. This is presumably a pyridinium salt, since it does not belong to the cubic system, and cannot be distinguished after the preparation has been dried.

EXPERIMENTAL.

The following solutions are required : 2N-Nitric acid, N/50-silver nitrate, and 3 concentrations of ammonia, *viz.*, " strong " (*d* 0·88), " medium " (strong solution diluted with 5 vols. of water), and " weak " (dilution of strong by 100 vols. of water).

Method.—On the micro-slide, place a small drop (approx. 0·02 ml.) of the test solution derived from the usual fusion, make it just acid with 2N-nitric acid, add a large drop (approx.

0·1 ml.) of N/50-silver nitrate solution, and evaporate the mixture just to dryness in order to prevent loss of silver chloride in subsequent filtration. Wash the residue twice by adding a drop of distilled water, warming, stirring, and removing the liquid with a hair-tip capillary (C. L. Wilson, " An Introduction to Microchemical Methods," 1938, 41). With small precipitates, loss may be avoided by sealing the tip of the capillary, centrifuging, and returning any solid to the bulk. Again evaporate the test drop just to dryness, cool it on a metal block, and extract it with a large drop of weak ammonia, stirring well. Filter the solution by a capillary, and blow out the *clear* liquid on to as small an area as possible on a slide, best by blowing out a tiny drop at a time and drying between the addition of each droplet. When the residue is quite dry and cool, dissolve it in the minimum volume of strong ammonia, cover the solution with a cup, and set it aside (Drop A).

Wash the residue from the test drop twice with a large drop of medium ammonia, stirring well and filtering off the wash liquid each time. Extract the residue with strong ammonia, filter the extract, blow out the *clear* liquid on a slide, cover it, and set it aside (Drop B). Wash the residue thoroughly twice with strong ammonia, and filter. Dissolve the residue in a drop of pyridine, stir well, and set the clear liquid aside (Drop C).

Examine A, B and C after crystallisation has proceeded considerably (usually 2—5 mins.) but do not let the drops become dry. A magnification of 200 is recommended. The appearances to be expected are described in tabular form.

Halide.	Drop A.	Drop B.	Drop C.
Cl	Octahedra, squares and cubes (Note 1)	Nil, or trace of dust	Nil
Br	Dust. May show triangles and hexagons (Note 2)	Many large triangles and hexagons. Field clear	Nil
I	Nil	Nil or dust	Characteristic pyridinium salt crystals (Note 3)
Cl and Br	Small squares, cubes, nodules (Note 4)	Many triangles and hexagons. Field fairly clear	Nil
Br and I	Dust. May show triangles and hexagons	Triangles and hexagons. Field clear, or dust	Characteristic pyridinium salt crystals
Cl and I	Octahedra, squares, cubes	Nil, or dust	Characteristic pyridinium salt crystals
Cl, Br, and I	Small squares, cubes, nodules	Many triangles and hexagons. Field fairly clear or dust	Characteristic pyridinium salt crystals

Notes on Table.—1. The chloride crystals normally grow to large, highly refractive octahedra, cubes, or squares (depending on the concentration) which appear perfectly clear, but often exhibit one or more dead black faces under the microscope.

2. Many of the hexagons and triangles are large, and although not necessarily regular, most of them are well formed, with sharply defined edges. Re-entrant angles can be seen occasionally. Colours vary. Sometimes preparations are obtained in which all the crystals are a strong blue-grey, but frequently preparations result in which the crystals show delicate pink, green, mauve, and yellow colours.

3. These crystals are transparent oblong shapes with frequent deep V-shaped re-entrants at the ends. They often occur in pairs, crossed, or in clumps, piled on top of each other spirally round a vertical axis, giving a very characteristic appearance. Under the polarising microscope they show strong double refraction, with parallel extinction.

4. Numerous transparent small squares, and crystals of square outline, which are invariably seen when the preparation has been treated as described above, are the characteristic proof of the presence of chloride.

Discussion.—It will be gathered from the table and notes that there is no difficulty in distinguishing between chloride and bromide occurring alone in solution, and iodide in any circumstances. The most difficult part of the test is the identification of chloride and bromide occurring together. This requires considerable care, but practice with known solutions soon enables the technique to be acquired; failing this, the tests should be carried out in duplicate.

At each stage in the test absence of further halogens will be indicated by complete dissolution of the residue.

Since the test is perfectly simple when only one halide is known to be present, this is easily the most satisfactory method for most organic compounds. The extension of the test to all three halides makes it of great value in inorganic analysis also.

The sensitivities of the tests for chlorine, bromine, and iodine when occurring separately are really only limited by the solubilities of the silver salts. In fact, a positive test for chloride may be obtained when no precipitate can be observed on addition of silver nitrate. Consequently 1γ of the elements can be detected comparatively easily. In mixtures it is possible to recognise one part of chloride in the presence of 10 of bromide, one part of bromide in the presence of 30 of chloride, and one part of iodide in the presence of 50 of either of the other two.

If a considerable amount of material is available, these limits can be extended further by concentrating fractions, which are then treated in the normal way.

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