

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE MICRO DETERMINATION OF HALOGENS AND METALS IN ORGANIC COMPOUNDS

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Hitherto, the Carius method has been the only accurate one available for the determination of halogens in all types of solid and liquid organic compounds. The method recently described by Thompson and Oakdale¹ has proved so accurate and satisfactory, even in the case of volatile liquids, that it seemed desirable to apply it to the micro determination of halogens. For the micro procedure we have devised a much more compact apparatus and as a result the method has become simpler and more rapid. A complete analysis, from the time of weighing the sample until the weight of silver halide is obtained, requires only forty-five to sixty minutes.

The principle involved is, as stated previously,¹ the use of fuming sulfuric acid as oxidizing agent, to which in certain instances persulfate is added. Any halide formed is then oxidized by permanganate or hydrogen peroxide to free halogen, which is absorbed in alkaline arsenite and subsequently precipitated as silver halide.

The micro determination is so simple, rapid and accurate that it seems likely to replace the classical Carius method.

Experimental

The samples used weighed 15–25 mg. A micro balance was not required and weighings accurate to 0.01 mg. were quickly made on a Bunge air damped balance, type 4 DM, with a capacity of 200 g.

The apparatus used, which is made entirely of pyrex glass, is shown in Fig. 1. It consists of a 25-cc. flask provided with two small condensers and connected to two absorption bulbs by means of ground-glass joints, 7 mm. inside diameter. A small dropping funnel is fused to the top of the condenser.^{1a} For much smaller samples the size of the apparatus can be reduced.

The Determining of Chlorine and Bromine.—If the compound is a solid, a sample of approximately 20 mg. or less is weighed into a micro beaker, about 6 × 7 mm., made from pyrex glass tubing. The sample and beaker are transferred to the decomposition flask

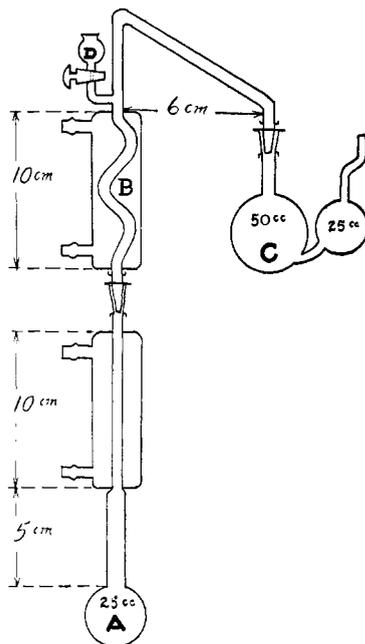


Fig. 1.

¹ Thompson and Oakdale, *THIS JOURNAL*, 52, 1195 (1930).

^{1a} This apparatus can be purchased from the Arthur H. Thomas Co., Philadelphia.

(A), Fig. 1. Five-tenths g. of potassium persulfate is then added² together with a few glass beads and a little copper sulfate. Section (B) is connected, and water passed through the condensers.³ The absorption flask (C) contains 0.1 g. of arsenic trioxide to reduce halogen to halide,⁴ 1 g. of chlorine-free sodium hydroxide and 15 cc. of water. Through the dropping funnel (D) 4 cc. of fuming sulfuric acid containing 20% SO_3 is added and the mixture is allowed to digest for fifteen minutes, keeping the sulfuric acid boiling gently. Then 5 cc. of concd. sulfuric acid (sp. gr. 1.84) is added. After the acid has become colorless and while it is boiling gently, an excess of a saturated solution of permanganate is added (2 cc. is usually sufficient), then 5 cc. of water. At this stage the condensers are emptied and the solution boiled until sulfur trioxide fumes appear. The apparatus is disconnected immediately, to prevent the joints from freezing, the contents of the absorption flask are transferred to a 100-cc. beaker and neutralized with dilute nitric acid (sp. gr. 1.10), using methyl orange as indicator. An excess of silver nitrate is added, then concd. nitric acid (sp. gr. 1.42) until there is an excess of 2 cc. The solution is boiled to coagulate the silver halide and filtered through a filtering crucible with a porous porcelain bottom,⁵ washed with 1% nitric acid, then with acetone, dried at 135° and weighed.

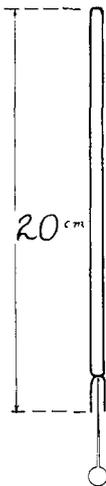


Fig. 2.

When liquid halogen compounds are to be analyzed, thin-walled bulbs are prepared. A bulb is filled by placing it and the liquid in a special apparatus.¹ The apparatus is evacuated through a side arm and then upon allowing the air to enter the apparatus the bulb is filled. Since the latter is too light to break by falling, it must be crushed somehow. A pyrex glass tube sealed off at both ends but having a pocket on one end to hold the stem of the bulb is used for this purpose (see Fig. 2). The bulb stem is placed in the pocket and then inserted into the flask which already contains the sulfuric acid, etc., and which is held horizontally. Care must be taken that the bulb does not fall out of the pocket. Both tube and crushed bulb are left in the apparatus until the determination is completed.

When chloroform or carbon tetrachloride is analyzed by this process, gaseous halogen compounds escape before complete reaction with sulfur trioxide occurs. This difficulty is surmounted by placing a narrow-bore quartz tube, about 20 cm. long, between the condenser and decomposition flask. Connection is made by heavy black rubber tubing. Heating the central portion of the tube to a red heat decomposes any organic halide gas and the halogen is completely absorbed.

The results of analyses of chlorine and bromine compounds are shown in Tables I and II. All the compounds used in this work were specially purified.

Determination of Iodine.—The procedure is identical with that for chlorine and bromine, except that no persulfate is added and an excess

² Since the persulfate is usually contaminated with perchlorate, some of it being quite unfit for use, a blank determination is made, using a halogen-free organic compound, such as starch.

³ All joints are well lubricated with a viscous paste, made by mixing phosphorus pentoxide with warm, sirupy phosphoric acid. See also Stephens, *THIS JOURNAL*, **52**, 635 (1930). Rubber bands are used on the glass hooks.

⁴ Hönigschmid and Zintl, *Ann.*, **433**, 201 (1923).

⁵ These crucibles (type A1 is densest) are manufactured by the Staatliche Porzellan Manufaktur, Berlin. They were cut down to a height of approximately one centimeter and then weighed about 3 g.

TABLE I

Substance analyzed	Sample, mg.	AgCl, mg.	Chlorine, %	
			Calcd.	Found
CHCl ₃	18.96	68.20	89.10	88.98
CHCl ₃	28.71	103.27	89.10	88.98
CCl ₄	14.64	54.57	92.20	92.20
CCl ₄	12.96	48.28	92.20	92.15
CH ₃ CONHCl	18.16	27.76	37.92	37.81
CH ₃ CONHCl	19.21	29.41	37.92	37.87

TABLE II

Substance analyzed	Sample, mg.	AgBr, mg.	Bromine, %	
			Calcd.	Found
C ₂ H ₅ Br	35.66	61.41	73.34	73.29
C ₂ H ₅ Br	14.58	25.08	73.34	73.22
C ₂ H ₂ Br ₄	25.06	54.42	92.47	92.41
C ₂ H ₂ Br ₄	18.59	40.29	92.47	92.23
CHBr ₃	21.02	46.86	94.85	94.87
CHBr ₃	25.03	55.76	94.85	94.80

of halogen-free 10% hydrogen peroxide is used instead of permanganate. If persulfate is used, oxidation to non-volatile iodic acid occurs. The oxygen liberated from the peroxide expels the iodine from the apparatus and the hydriodic acid usually present is oxidized to free iodine. When a substance containing a very high percentage of iodine, such as iodoform, is analyzed in this way, some iodic acid is formed, due to insufficient organic reducing material. This may be remedied in either of two ways: first, by preventing the formation of iodic acid by adding 0.05 g. of starch to the iodine compound before decomposition begins; or, second, if iodic acid is formed, it is reduced, after all the iodine has been expelled from the apparatus, by adding a solution of hydrazine sulfate, followed by an excess of peroxide. For iodine determinations the dropping funnel (D) is conveniently sealed at the top of condenser (A) instead of (B).

TABLE III

Substance analyzed	Sample, mg.	AgI, mg.	Iodine, %	
			Calcd.	Found
CHI ₃	22.52	40.24	96.70	96.60
CHI ₃	26.06	46.59	96.70	96.64
C ₁₂ H ₁₀ SbI	19.31	11.24	31.51	31.51
C ₁₂ H ₁₀ SbI	17.98	10.47	31.51	31.48
C ₁₂ H ₁₀ AsI	22.24	14.66	35.66	35.63
C ₁₂ H ₁₀ AsI	19.59	12.92	35.66	35.65

Micro Determination of Metals in Metallic Organic Halides.—If metals are to be determined the procedure is the same except that copper sulfate need not be added. Arsenic was determined in diphenylarsyl iodide in the

following manner. The residual liquid in flask (A) after removal of halogen was transferred to a 150-cc. conical flask, the arsenic pentoxide was reduced to the trivalent state with sulfur dioxide, the solution diluted to 75 cc., boiled to remove the excess, 10 cc. of concd. hydrochloric acid was added and the arsenic trioxide titrated at 80° with *N*/100 potassium bromate, using methyl orange as indicator.⁶

If only arsenic is to be determined it is best to decompose the compound and reduce the arsenic entirely in the original flask (A). The iodine is expelled with 30% hydrogen peroxide and the arsenic pentoxide is reduced by adding an excess of solid hydrazine sulfate,⁷ which in turn is destroyed by heating the solution to 250° for ten minutes. Antimony in diphenylstibyl iodide is determined in the same manner as the arsenic. The results are shown in Table IV.

TABLE IV
RESULTS OF ANALYSES

Substance	Sample, mg.	Metal present, %	Found, %
C ₁₂ H ₁₀ SbI	22.18	30.23 Sb	30.05
C ₁₂ H ₁₀ SbI	20.32	30.23 Sb	29.98
C ₁₂ H ₁₀ AsI	19.59	21.05 As	21.25
C ₁₂ H ₁₀ AsI	34.03	21.05 As	20.96
Selenium and CHBr ₃	26.42	97.87 Se	97.72

It seemed desirable to apply this method to the determination of selenium in organic compounds containing halogens. Because no organic compound containing selenium was available, pure selenium powder was mixed with bromoform and the mixture decomposed by heating with 2 cc. of fuming and 3 cc. of concd. sulfuric acid. The bromine was liberated by permanganate and absorbed as usual. The selenic acid remaining in the flask was determined by reduction to metallic selenium⁸ with an excess of hydroxylamine hydrochloride and determined gravimetrically. No volatilization of selenium occurred in the presence of bromine. Results are shown in Table IV.

Summary

1. A micro method has been described for the determination of halogens in solid or liquid organic compounds, based upon oxidation of the sample with fuming sulfuric acid. The halogen is distilled into alkaline arsenite and then precipitated as silver halide.

⁶ Györy, *Z. anal. Chem.*, **32**, 415 (1893). Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., N. Y., 1929, Vol. II, p. 580. This is simpler and more rapid than the method suggested by Cislak and Hamilton [*THIS JOURNAL*, **52**, 637 (1930)] and equally accurate.

⁷ Schulek and Villecz, *Z. anal. Chem.*, **76**, 81 (1929).

⁸ Lenher and Kao, *THIS JOURNAL*, **47**, 2454 (1925); Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 265.

2. Metals may be determined in the same solution from which the halogen has been removed.

3. A more compact apparatus can be used and the whole process is simpler and more rapid than in the macro method previously described.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH]

AN APPLICATION OF MOVING BOUNDARIES TO A STUDY OF AQUEOUS MIXTURES OF HYDROGEN CHLORIDE AND POTASSIUM CHLORIDE

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Introduction

The purpose of this research was the measurement of the mobilities of the various ion constituents in aqueous mixtures of hydrogen and potassium chlorides. Since the conductances of such solutions do not follow the law of mixtures, it appeared of interest to determine which ion constituents were responsible for these deviations. The moving boundary method was employed in these determinations, boundaries of the rising type being used exclusively. The results, as will be shown below, are also of interest in connection with the recent work on the separation of the rare earth elements by the ionic migration method.²

Theoretical

The electrolysis of a mixture of hydrogen and potassium chlorides, using, for instance, a cadmium anode as the source of indicating cations, may be represented diagrammatically as follows. The use of the metallic anode in this manner is the method of Cady and Longworth,³ though the source of indicating ions may also be a solution of an appropriate electrolyte. Both methods were employed in these experiments. The tube is initially filled throughout with the mixture of uniform composition as shown in Fig. 1. After current has passed for a time, the hydrogen-ion constituent originally in the lower part of the tube will, due to its high mobility, have forged ahead of a portion of the potassium-ion constituent, and there should be the two boundaries, A and B, as shown in Fig. 2. These two boundaries have been observed and their separate progress has been followed quantitatively.

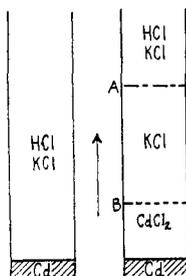


Fig. 1.

Fig. 2.

¹ National Research Council Fellow.

² Kendall and Clarke, *Proc. Nat. Acad. Sci.*, **11**, 393 (1925); Kendall and Crittenden, *ibid.*, **9**, 75 (1923); Kendall and White, *ibid.*, **10**, 458 (1924).

³ Cady and Longworth, *THIS JOURNAL*, **51**, 1656 (1929).