Davis[1] purified ordinary lead and lead from samarskite by crystallization of the nitrate and chloride. Analysis of the chloride gave the value 207.27 for the atomic weight of common lead and 206.30 for that of radioactive lead.

The samarskite was found to contain 12.21% uranium and 1.03% thorium.

J. J. van Laar[2] applies a method of critical constants to the determination of the atomic weights of several elements, using the density data of various experimenters, with the following results: H = 1.00770; He = 4.000; C = 12.001; N = 14.004; S = 32.060; Cl = 35.460; Br = 79.922.

Moles[3] discusses critically revisions of atomic weights published in 1917.

Guye and Renard[4] consider the distribution of errors in determinations of atomic weights.

Guichard[5] briefly compares methods of atomic weight investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A SIMPLE, RAPID METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC SUBSTANCES.[6]

BY W. A. VAN WINKLE AND G. McP. SMITH.

Received November 22, 1919.

Introduction.—The present investigation is a continuation of work taken up by G. McP. Smith at the request of the Bureau of Mines shortly after our entry into the war, which led to a scheme for the rapid, approximate determination of certain gases (*e. g.*, of chloropicrin) in the air by a method of simple combustion.

In view of the difficulties involved in many of the available methods for the determination of halogen in organic compounds, this method of simple combustion was considered worthy of further investigation. And it will be shown in the experimental part that the method in its simplest form is capable of wide application, and that it can be depended upon to furnish reliable values.

Previous Work.—This method of analysis has frequently been proposed, and nothing could be simpler in principle. Trouble has always been met with, however, in carrying out the combustion, and often in

[1] *J. Phys. Chem.*, **22**, 631 (1918).

[2] *J. chim. phys.*, **17**, 266 (1919); *Chem. Weekblad*, **16**, 1243 (1919).

[3] *J. chim. phys.*, **16**, 350 (1918).

[4] *Arch. sci. phys. nat.*, **44**, 402 (1918).

[5] *Bull. soc. chim.*, **21**, 238 (1917).

[6] Excerpt from a thesis submitted to the Graduate Faculty of the University of Illinois by W. A. Van Winkle, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

determining halogen in the combustion products. Some of the procedures require a combustion tube to be packed with substances which may fuse upon the glass, and many require close attention throughout the combustion.

Warren[1] burns the substance in a stream of oxygen, absorbing the halogen with various oxides, as zinc oxide, lead dioxide and cupric oxide, placed forward in the tube. The halogen is extracted from the oxide with sodium carbonate solution, and is determined in the extract. Only chlorine compounds were studied, and the results leave much to be desired.

Brügelmann[2] also burns the substance in oxygen, but uses calcium oxide to absorb the halogen; otherwise his procedure is much the same, except that he titrates according to Volhard, and obtains values better than Warren's.

Dennstedt[3] recommends burning in oxygen, with platinum black as a catalytic agent, and absorbing the halogen with lead dioxide in the case of chlorine or bromine compounds, and with metallic silver in the case of iodine compounds. With lead dioxide, he follows Warren's subsequent procedure; with silver, the increase in weight is ascribed to iodine.

Plimpton and Graves[4] introduce the vaporized organic halogen compound into the flame of a specially constructed Bunsen burner, when the halogens are obtained in combination with hydrogen, and also in the free state. The products are absorbed in sodium hydroxide solution, and after reduction the halogen is precipitated with silver nitrate. Apparently it is not easy to control the combustion, which must be given constant attention. Good values are given for about 10 compounds.

Zulkowsky and Lepéz[5] burn the organic substance in a stream of oxygen with platinized quartz as a catalyst. In the case of chlorine compounds, they use ammoniacal hydrogen peroxide as the absorbing agent, and in that of bromine or iodine compounds, a solution of potassium iodide. With the latter solution, the determination is iodometric. Chlorine compounds present difficulties, since the platinum tends to retain chlorine, which is wholly removed only with excessive heating. Their method is complicated, but they find good values in most of the analyses, which check well with figures obtained by the Carius method.

Klason[6] suggests burning the substance in a stream of air or oxygen mixed with nitrous fumes, the latter being introduced ahead of the sample, and the burning taking place in the presence of platinum foil. In

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[1] *Z. anal. Chem.*, 5, 174 (1866).

[2] *Ibid.*, 15, 1 (1876); 16, 1 (1877).

[3] *Ber.*, 30, 1590 (1899).

[4] *J. Chem. Soc.*, 43, 119 (1883).

[5] *Monatsh.*, 5, 537 (1884).

[6] *Ber.*, 19, 1910 (1886).

the case of bromine or chlorine compounds, he recommends passing the products into silver nitrate solution; with iodine compounds, into water, the iodine being taken into solution with sulfurous acid, the liquid neutralized, and the iodine precipitated with silver nitrate. No analytical data are given.

Reid[1] burns the sample in a boat using a slight excess of oxygen, and absorbs the products near the exit of the combustion tube, at about 270°, with finely divided silver and silver oxide, contained in a small silver boat. After the combustion Reid reduces the residual silver oxide at a temperature of about 170° by means of a current of hydrogen. Having the weight of the silver boat plus the finely divided silver, of the boat and silver plus the silver oxide, and of the boat and its contents after absorption and reduction, "To find the weight of the halogen absorbed, deduct from the weight of the silver boat containing the oxide, the amount that this oxide would lose on reduction, and subtract this corrected weight from the final weight of the boat." The method, though complicated and requiring experience and care, appears to be capable of yielding good results.

Experimental.

Outline of Method.—The sample, carried by means of a current of air, is drawn through a strongly heated quartz tube, and the combustion products are passed into a suitable absorption vessel containing sodium hydroxide solution. Any oxyhalogen salts are then reduced and the halogen estimated by the Volhard method.

Development of a Suitable Furnace and Combustion Tube.—In the first experiments a 22 mm. quartz tube was heated in a 30 cm. Hoskins electric combustion furnace; but, owing to the time consumed in sweeping out the gaseous products, this tube was early replaced by one 6–7 mm. in diameter, and this size was adopted in the final apparatus. To allow a better control of the combustion process, a longer furnace containing 3 separate 25 cm. heating units was designed and built. This furnace could be heated in sections, as desired, the middle unit being so constructed as to permit of its use either as a 12.5 cm. or as a 25 cm. unit. In this way, 12.5, 25, 38, 50 and 75 cm. lengths of the furnace could be brought into action.

In over 100 determinations made with these furnaces, mostly with chloroform,[2] it was found that if the ratio of air to volatile material was not

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[1] THIS JOURNAL, 34, 1033 (1912).

[2] The lowest satisfactory combustion temperature in the case of chloroform, with the use of air, appears to be about 900°. For example, with a sample containing 88.4% of chlorine (mean of 7 Carius determinations), the following results were obtained (30 cm. furnace): 900°, 88.60%; 850°, 88.45%; 800°, 84.97%; 750°, 78.90%. At about 600°, particularly with a slow current of air, an appreciable deposit of fine needle-like crystals settled in the cool portion of the tube. Recrystallized from alcohol,

allowed to change suddenly in favor of the latter, due to excessive heating of the sample holder, the combustion could be depended upon to go smoothly, and without much attention. It was found advisable to place a thermometer beside the sample holder, and to warm both gradually (in a bath) to a temperature 10 to 30° below the boiling point of the sample.

A few runs made with tank oxygen showed no improvement over air.

Although it was possible to obtain good results with chloroform and carbon tetrachloride, with the use of these furnaces, the first bromine compound studied, ethyl bromide, revealed a serious defect in the apparatus. Heavy bromine vapors condensed in the projecting end of the tube, and could not be completely removed without undue trouble and loss of time. At this point it was found that the operation could be materially simplified, and much time saved, by means of the gas-heated tubes to be described later (see Fig. 1). Combustion furnaces of the ordinary, slow-cooling, type were therefore discarded.

Sample Holders and Absorption Tubes.—Many types of sample holder were tried, several with success, but the most reliable are those shown in Figs. 1 and 2. And, while several types of absorption apparatus gave good results, the type finally adopted is considered decidedly superior for this work. It is illustrated in Fig. 1.

Reduction of Oxy-halogen Salts, Precipitation, and Titration.—Before precipitating the halogen in the absorption liquid, it is of course necessary to reduce the oxy-halogen salts which are present. For this purpose, hydrogen peroxide, metallic zinc, and sodium sulfite were studied.

Using a known weight of carefully purified potassium chlorate as a standard, and reducing with sodium sulfite, each of 8 gravimetric determinations yielded the theoretical weight of silver chloride. This reagent was therefore adopted. But before the addition of silver nitrate it is, of course, necessary to remove the excess of the sulfite. This was originally accomplished by boiling the slightly acidified solution; but so much time was consumed in this operation that oxidation by means of potassium permanganate was substituted. Test analyses showed the two methods to be about equally accurate.[1]

The procedure finally adopted is as follows: The absorption solution was made up in each instance by mixing 25 cc. of approximately 5 *N* sodium hydroxide solution and 10 cc. of 2 *N* sodium sulfite solution. If

these melted at 229° corr., and gave a copious test for chlorine; hexachlorobenzene was indicated.

As to the length of furnace heated, studies made at about 900° show that low values are likely if this is less than about 20 to 25 cm. Since the extremities of an electric combustion furnace fall off decidedly in temperature, this means the use of 30 to 38 cm. heating coils.

[1] Using pure NaCl, KBr, and KI as standards, adding Na_2SO_3, acidifying with dil. H_2SO_4, and comparing the two methods, the following values were found by the

these reagents were not halogen-free, the quantities used were accurately measured by means of pipets, since, in that case a correction had to be made in accordance with the results of duplicate blanks run with the absorption solution alone.[1]

After absorption, the solution was treated with 25 cc. of dil. sulfuric acid, and the excess of sulfite oxidized with permanganate solution, added to the appearance of a faint pink color. Standard silver nitrate solution was then added, about 5 cc. in excess, followed by a few cubic centimeters of dil. nitric acid; if, on shaking for a few moments, the precipitate did not coagulate, the suspension was warmed on the steam bath. The precipitate was filtered in the cold with suction and washed with 1% nitric acid, even in bromine and iodine determinations, since the sodium hydroxide and sulfite of commerce contain traces of chloride. Finally, 5 cc. of ferric alum indicator was added to the filtrate, followed by enough dil. nitric acid to lighten the color, and the solution was then titrated with standard thiocyanate solution, of half the normality of the silver solution used.[2]

For the sake of uniformity, all titrations were carried out in artificial light, and for this purpose a special titration table was designed and constructed. With the burets mounted upon this table, the titration was performed in the light from two 100-watt, nitrogen-filled, blue glass (or daylight) lamps, one behind each buret, in a compartment lined with asbestos board, but faced with ground glass. The base beneath the burets was of glass, with its under side covered with white (lithopone) paint. A special lamp was provided to facilitate reading the burets.

Check Analyses.—Owing to the difficulty of always obtaining pure organic compounds, it was decided to check the combustion results by some standard method of analysis, and for this purpose the Carius method was selected, in spite of its drawbacks, as being the most reliable.

Volhard method. (The NaCl to which no sulfite was added was analyzed gravimetrically. This salt was used in standardizing the silver nitrate solutions employed throughout the work.)

	Sulfite boiled off.	Sulfite oxidized.	No sulfite added.
NaCl..........	60.45–60.66% Cl (8 determinations)	60.42–60.71% Cl (5 determinations)	60.63 and 60.65% Cl (gravimetric)
KBr..........	67.58 and 67.59% Br	67.71 and 67.68% Br	67.55 and 67.54% Br
KI...........	76.66% I	76.69 and 76.63% I	76.51 and 76.55% I.

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[1] By preparing these reagents in quantity, it is unnecessary to make repeated blank runs. In this investigation halogen-free reagents were used at the start, but it was later found more convenient and just as accurate to use the ordinary stick sodium hydroxide and the sodium sulfite of commerce.

[2] The dil. H_2SO_4 and HNO_3 are made by mixing one vol. of conc. acid with 3 vols. of water. The $KMnO_4$ solution used to oxidize the sulfite is a saturated solution of the salt. The indicator is made by adding conc. HNO_3 to a saturated solution of ferric alum, to the complete lightening of the deep brown color. The standard solutions recommended are 0.1 *N* and 0.2 *N* $AgNO_3$, and 0.05 *N* and 0.1 *N* thiocyanate, depending upon the quantity of halogen to be precipitated.

For use with this method, an electrically heated multiple and continuous bomb furnace was designed and constructed. This furnace, which will be described elsewhere in detail by W. A. Van Winkle, consisted in brief of six 5 cm. iron pipes, each about 1.5 meters in length, bound together in an upright bundle by 3 iron bands, and heated by several well insulated coils, which surrounded the lower half of the bundle, as well as by a heating element placed at the base, and one in the center of the bundle, the whole encased in a box of 12 mm. transite asbestos board. By means of pulleys suspended overhead from a framework, six 32 mm. counterpoised iron pipes, or bomb containers, could be lowered into the heated zone of the 5 cm. pipes. Thus, 6 bombs could be introduced independently into or withdrawn from the furnace, and the latter could be operated continuously, since with the upper half of the furnace not directly heated the bombs could be lowered or raised gradually, without a sudden change of temperature. Four thermometers, permanently installed at different heights, together with various permutations of electrical connections, facilitated the easy maintenance of satisfactory temperatures.

Description of the Apparatus Used with Volatile Substances.—This apparatus is illustrated in Fig. 1. We wish to emphasize at the start that with the use of several Bunsen burners, with wing tops set lengthwise of the combustion tube as shown in the figure, and employing the hottest blue flame possible, it was easy to maintain a temperature of nearly 1000°,

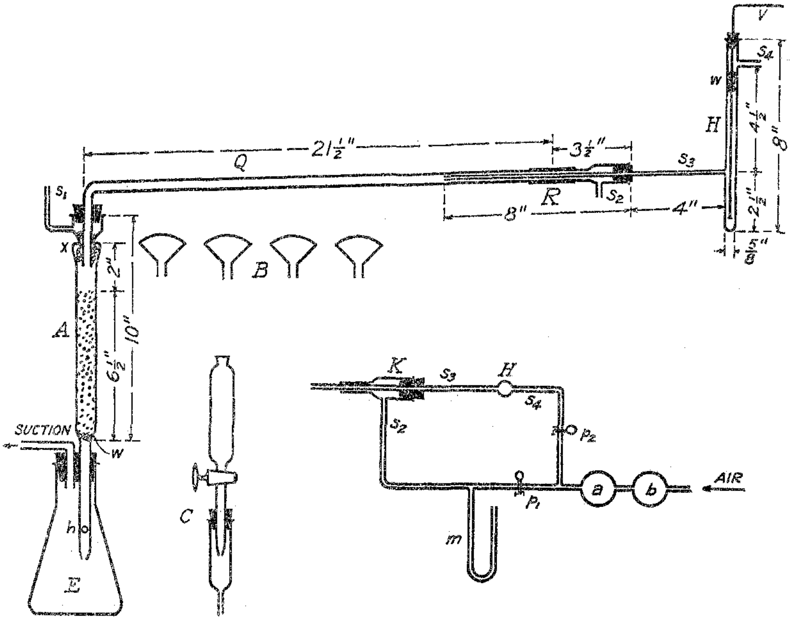

Fig. 1.

especially if an inverted V-shaped reflector of asbestos board were suspended about an inch above the tube.

The sample holder H was a Pyrex test-tube, 200 × 16 mm., provided with two side arms of one mm. bore, one, S_4, for the entrance of air, and the other, S_3, for the exit of air mixed with volatilized sample, this mixture being discharged into the combustion tube far beyond the rubber connection which held the glass adapter K against the quartz combustion tube. The glass rod V was carefully worked downward through the rubber stopper to break the small, glass sample bulb at the bottom of the holder. To protect the rubber stopper of the holder from attack by the organic substance a tightly fitting plug of glass wool was placed just below the side arm S_4.

A washing bottle containing conc. sulfuric acid and a soda-lime tower used to insure the introduction of pure air, are represented in the figure by *b* and *a*, respectively; *m* is a water manometer. Pinchcocks are indicated by P_1 and P_2. By means of small rubber tubing, *b*, *a*, S_4, S_2, and *m* were connected up as shown.

The combustion took place in a 60 cm. quartz tube,[1] Q, of 6 mm. bore, which was slightly inclined towards, and extended down into the absorption apparatus A. Any bromine or iodine condensing near the exit of the tube was later washed over into the absorption vessel, by removing the rubber stopper of K, and introducing water into Q, slight suction being maintained the while.

The absorption vessel A was a piece of glass tubing, 25 cm. long and of 25 mm. outside diameter, into which the absorbing solution continuously flowed through S_1. About 38 mm. from the upper end the tube was constricted in such a way as to direct the solution towards the combustion tube and cause it to flow down the outside of the latter and drip off its end. Glass wool, packed in the constricted area and also wrapped loosely over the end of the combustion tube, was kept moist by the absorption liquid and thus effectively prevented any loss of halogen by contact with the rubber stopper above. At *w* there was placed a thin layer of glass wool, and above this a 15 to 18 cm. column of sea sand, previously digested with alkali and acid. The extension tube leading into the 500 cc. Erlenmeyer flask E had a small perforation, *h*, about an inch above its lower end, which allowed the residual gases to escape and the liquid to drop smoothly from the end of the tube. A small dropping funnel containing 25 cc. of sodium hydroxide solution, 10 cc. of sodium sulfite solution, and about 15 cc. of water, was supported so that the adapter C could be connected readily to the side arm S_1 by a short length of rubber tubing. The dropping of the liquid from the stem of the funnel,

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[1] While a tube of transparent quartz is to be preferred, it was not necessary, both transparent and opaque tubes have been used with success.

constricted at the end to about 2 mm., afforded an indication of the rate of flow of the alkaline sulfite solution into the absorption apparatus.

A guard bottle (not shown in the figure), with an entrance tube of 3 mm. bore, and containing water, to serve as a bubble counter, was placed between the Erlenmeyer flask and the suction pump.

Procedure for Carrying Out the Combustion and Absorption.—About 0.25 g. of material to be analyzed was weighed out in a small, sealed bulb, and placed in the lower end of the holder, ready to be liberated at the proper time by breaking the bulb. The apparatus was then set up and adjusted as described, with the absorption solution in the dropping funnel, an asbestos shield to protect the absorption tube and its rubber stopper from the heat of the burners, and an inverted V-shaped asbestos heat-reflector; and the burners were lighted and adjusted. The pinchcocks P_1 and P_2 were opened, the water pump and the flow of the absorption solution started from C (the sand in A should become thoroughly soaked with this liquid, before it is reached by the products of combustion). The suction was so adjusted that bubbles passed the counter at the rate of 200 per minute, and the cock of the dropping funnel so that the liquid ran at the rate of 20 to 30 drops per minute. This kept the sand well soaked with fresh reagent.[1] The pinchcock P_2 was then tightly closed, but P_1 left wide open, and the bulb holding the sample was broken. If, after a couple of minutes, no fog appeared above the sand, the pinchcock P_2 was opened slightly; in this way there was no danger of carrying an excess of the volatile sample into the combustion tube. It was necessary that the manometer should always show a negative pressure within the apparatus, of 2 to 6 in. of water. By closing P_2 at any time, the change in level of the liquid gave a rough indication of the relative volumes of air flowing through the two entrances of the combustion tube.

With a substance like ethyl bromide, boiling at 38.4°, it was unnecessary to warm the holder until near the end, when a free flame was cautiously applied to volatilize the small quantity of liquid usually held within the capillary of the sample bulb. Less volatile substances required a gentle warming of the holder at 10 to 30° below their boiling points. In all cases, after once regulating the combustion so that a slight fog continuously hovered above the sand in the absorption vessel, very little attention was required until near the end of the operation.[2]

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[1] If, towards the end, it appeared that not enough solution was left to last out the run, some water was added; the reagent was sufficiently concentrated to permit the addition of 1 to 2 parts of water.

[2] Sometimes a small blue flame appeared at the end of the capillary side arm S_3. It was then advisable to close down P_2, and to open up P_1; and, in addition, if the holder was being warmed, to withdraw this source of heat. In the preliminary experiments with this apparatus, a much shorter capillary side arm, S_3, was used, until in one instance the small blue flame flashed back, and the holder broke. The substitution of a holder with a 30 cm. side arm prevented further trouble from this source.

When no further fog appeared above the sand, a free flame was applied to the holder, and the latter gradually heated until well above the boiling point of the substance. The burners were then turned out, the asbestos reflector and shields and the apparatus allowed to cool without discontinuing the suction. Within about 10 minutes, the contents of the combustion tube were rinsed into the absorption apparatus by means of a stream of water introduced through the adapter K. The absorption train was then disconnected, and the end of the combustion tube similarly washed, inside and out. Any reagent still in the dropping funnel was allowed to run rapidly through the glass wool into the absorption apparatus, and the latter was washed with a few small portions of hot water, the sand being sucked nearly dry after each addition of liquid.[1] The volume of liquid in the flask was then about 175 cc. It was cooled, if warm, 25 cc. of dil. sulfuric acid added, and the excess of sulfur dioxide completely oxidized with the least possible quantity of permanganate solution. The halogen was then determined by the Volhard method, as already described.

Analyses of Several Volatile Compounds.—Analyses of 12 volatile compounds, with the apparatus shown in Fig. 1, are recorded in Table I. Under Time, is given the number of minutes from the breaking of the sample bulb to the end of the combustion, including the final washing of the apparatus, and the tests for complete washing. In a few cases there was a failure to record the time, and in several the time noted is excessive, because, owing to the smoothness of the combustion, the operation was not closely watched, and more time than necessary was consumed.

Comparative analyses of the Carius method are recorded in the same table. The values obtained by combustion will speak for themselves; as compared with the Carius values, they were obtained with exceeding convenience and ease.

TABLE I.

Combustion.				Carius.		
No.	Sample. G.	Time. Min.	Halogen. %.	No.	Sample. G.	Halogen. %.
Ethyl bromide, C_2H_5Br (impure); b. p. of pure substance, 38.4°; Calc., 73.33% Br.						
1	0.3106	70	72.35	6	0.2479	72.24
2	0.3200	85	72.36	7	0.2244	72.07
3	0.2783	30	72.52	8	0.3027	71.67
4	0.3011	30	72.31	9	0.3225	72.34
5	0.2747	25	72.49	10	0.3370	71.78
		Mean,	72.43			72.02

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[1] In the case of iodine compounds, some iodine always solidifies in the end of the combustion tube, but this is without harm. When the tube is washed out, and the reagent remaining in the dropping funnel is run into A, the crystals of iodine are readily dissolved and carried into E.

TABLE I (*continued*).

Combustion.				Carius.		
No.	Sample. G.	Time. Min.	Halogen. %.	No.	Sample. G.	Halogen. %.
Chlorobenzene, C_6H_5Cl (pure); b. p., 132°; Calc., 31.52% Cl.						
11	0.3350	90	31.28	17	0.2304	31.17
12	0.2720	90	31.65	18	0.1982	31.26
13	0.2579	115	31.76	19	0.2721	31.75
14	0.2821	70	31.47	..	..	...
15	0.3034	95	31.70	..	..	...
16	0.3399	80	31.79	..	..	...
		Mean,	31.61			31.39
Ethyl iodide, C_2H_5I (impure); b. p. of pure substance, 72.2°; Calc., 81.34% I.						
20	0.4522	67	81.47	22	0.3028	81.47
21	0.4074	98	81.48	23	0.4750	80.90
..	..	...	...	24	0.2708	81.20
		Mean,	81.48			81.29
Bromobenzene, C_6H_5Br (pure); b. p., 157°; Calc., 50.90% Br.						
25	0.2520	...	51.01	28	0.3826	51.23
26	0.3147	...	50.93	29	0.3632	51.26
27	0.2802	120	50.83	..	..	...
		Mean,	50.92			51.24
Allyl bromide, C_3H_5Br (impure); b. p. of pure substance, 70°; Calc., 64.57% Br. (Sample difficult to get into bulb without decomposition.)						
30	0.2345	120	62.87	33	0.2141	61.02
31	0.2431	110	62.56	34	0.2252	61.70
32	0.2342	120	63.61	35	0.2842	62.12
		Mean,	63.01			61.61
Ethylene chloride, $C_2H_4Cl_2$ (pure); b. p., 83°; Calc., 71.71% Cl.						
36	0.2688	90	71.66	39	0.2773	71.68
37	0.2868	120	71.68	40	0.2414	72.04
38	0.2521	120	71.82	..	..	...
		Mean,	71.72			71.86
Butyl bromide, C_4H_9Br (impure); b. p. of pure substance, 100°; Calc., 58.34% Br.						
41	0.6136	128	58.16	44	0.2429	58.71
42	0.3231	58	58.14	45	0.2937	58.50
43	0.4751	123	58.11	..	..	...
		Mean,	58.14			58.60
Benzal chloride, $C_7H_6Cl_2$ (impure); b. p. of pure substance, 212°; Calc., 44.05% Cl.						
46	0.2965	90	44.51	50	0.2588	44.82
47	0.2332	90	44.41	51	0.2676	44.28
48	0.3049	75	44.47	..	..	...
49	0.2129	...	44.56	..	..	...
		Mean,	44.49			44.55

TABLE I (*continued*).

Combustion.				Carius.		
No.	Sample. G.	Time. Min.	Halogen. %.	No.	Sample. G.	Halogen. %.
Carbon tetrachloride, CCl_4 (pure); b. p., 78°; Calc., 92.20% Cl.						
52	0.2494	106	91.92	54	0.2321	92.50
53	0.2614	93	91.37	55	0.2805	92.02
..	..	...	...	56	0.2208	91.94
..	..	...	...	57	0.2813	92.63
		Mean,	91.64			92.54
Chloroform, $CHCl_3$ (impure); b. p. of pure substance, 61°; Calc., 89.02% Cl.						
58	0.2747	90	88.83	60	0.2430	88.28
59	0.2840	85	88.64	61	0.2485	88.20
..	..	...	...	62	0.2292	88.76
..	..	...	...	63	0.2449	88.48
..	..	...	...	64	0.2494	88.23
..	..	...	...	65	0.3004	88.39
..	..	...	...	66	0.3189	88.44
		Mean,	88.74		Mean,	88.40
Ethylene bromide, $C_2H_4Br_2$ (impure); b. p. of pure substance, 129°; Calc., 85.09% Br.						
67	0.3934	180	84.51	71	0.2800	84.45
68	0.2013	145	84.45	72	0.2955	84.59
69	0.2114	95	84.27	..	..	...
70	0.2178	105	84.41	..	..	...
		Mean,	84.41			84.52
Chloropicrin, CCl_3NO_2; b. p. of pure substance, 113°; Calc., 64.72% Cl. (An old sample in sealed tube prepared at Johns Hopkins University by R. W. Hale, Jr., and furnished through the Bureau of Mines.)						
73	0.3046	155	64.55	77	0.3443	64.14
74	0.1819	95	64.77	78	0.3448	64.47
75	0.2057	63	64.47	79	0.2946	64.53
76	0.2235	68	64.50	80	0.2342	64.60
		Mean,	64.57			64.44

The Analysis of Substances Containing More than One Halogen.—As has been pointed out by W. M. Dehn,[1] any two halogens in a binary mixture of halides may be calculated from the weight of the mixed silver salts, together with their silver equivalent as determined by the Volhard method. The possibility was studied of obtaining the necessary data for determinations of this class, by the combustion of the sample, followed by the determination in the one sample, of the two values indicated. But, although preliminary experiments gave promise of success, and the titration data obtained concerning the silver excess were very consistent, and probably correct, it was soon found that great difficulty would be encoun-

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[1] THIS JOURNAL, 31, 1273 (1909).

tered in the previous precipitation of the silver halides alone, for weighing, because the absorption solution in passing through the sand takes up silica, contaminating the silver halide precipitate. Solutions of pure sodium hydroxide and sulfite, prepared from metallic sodium, were also tried; but the quantity of silica obtainable from the acidified absorption solution, while somewhat less in amount, was still appreciable.

In the best of indirect methods, the analytical data must be exceedingly accurate if large errors are not to be introduced in the calculations; and, while in the present case a satisfactory solution of the difficulty might possibly be worked out, the matter was dropped for lack of time.

The Analysis of Difficultly Volatile Substances.—The results obtained with easily volatile substances led to a desire to apply the method to more difficultly volatile, or even to non-volatile, substances. A sample of material already analyzed by the Carius method was first studied. The apparatus at first used was that shown in Fig. 1; but it was found that the substance charred upon heating the holder, tarry material condensed in the side arm leading into the combustion tube, and it was impossible to volatilize this without burning the rubber connection and the stopper.[1] Nevertheless, success was indicated, provided an apparatus could be devised which would permit the burning of the condensed tarry material.

Accordingly, the apparatus was modified as shown in Fig. 2. The holder and combustion tube consisted of one piece of transparent quartz tubing, to which were fused the 2 mm. side arms S_2 and S_4, also of transparent quartz. A and B are top and side views, with lengths given to scale, and C is a diagrammatic sketch showing the connections of S_4, S_2, *m*, *b*, *a*, and the oxygen tank T. When in position for a combustion, the holder was not vertical in this case, but was inclined at an angle of 20° to the horizontal. In the case of solids, a boat was slid into the position shown; and the sample on melting ran to the bottom of the holder. In the case of liquids, a small sealed bulb was used, which was broken as already described; or, if the liquid was non-volatile, it was weighed out in a small quartz tube, which was slid into the holder.

The combustion was carried out as already described, but during combustion the aspiration was somewhat slower; with the introduction of oxygen, less residual gas passed through the absorption apparatus. In general, the pinchcock P_1 remained closed during the combustion, only air passing *via* P_2, and oxygen *via* P_3. Two or three times as much oxygen as air was used, the latter passing at the rate of about 100 small bubbles per minute. It was necessary that fog should form continuously above the sand in the absorption vessel, but should not become dense; this con-

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[1] In spite of these drawbacks, 4 determinations gave values ranging between 48.63 and 49.35% of Br, for a substance with a theoretical content of 50.29% (cf. Table II, which contains the final work on this compound).

dition depended largely upon the rate of aspiration, but also upon the rate at which oxygen was introduced. If the latter was slow and the former excessive, there was danger of charring. It was very easy, however, to regulate the flow of air and of oxygen, so that the sample volatilized and burned smoothly.

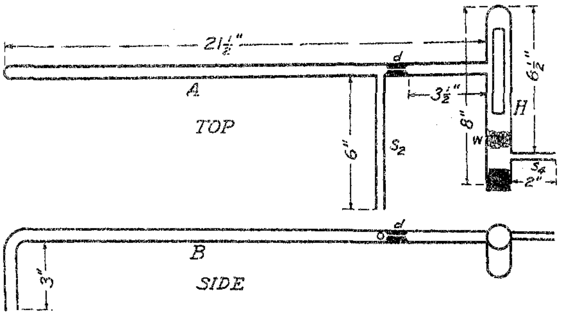

Fig. 2*a*.

These difficultly volatile substances required the direct heating of the holder; the initially small and steady flame was placed below the point midway between the plug of glass wool, *w*, and the entrance of the combustion tube. If a fog failed to appear shortly in the absorption vessel, the flame was increased, and if that did not suffice, the holder was covered below the flame with an inverted V-shaped asbestos reflector. Then, if the fog still did not materialize, the flame was gradually moved towards this reflector. But it was necessary to avoid charring the material, and thus setting free combustible gases too rapidly. Once having made the proper adjustments, the combustion proceeded smoothly, without much attention.

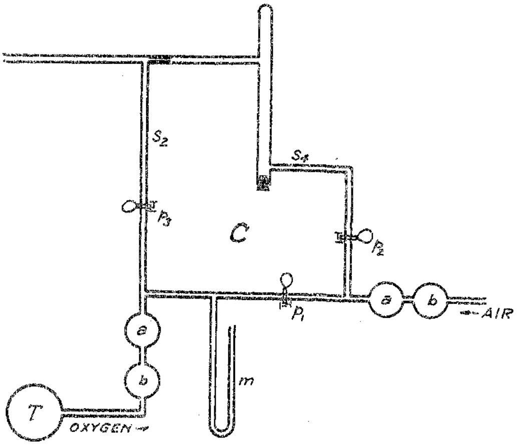

Fig. 2*b*.

Toward the close, the lower end of the holder was always coated with carbon. After heating the end carefully for a few minutes, with only air passing through H, the pinchcock P_1 was opened and P_2 closed. This let in pure oxygen, which readily burned off the carbon. The same applied to the heated deposit between H and *d* in the combustion tube. If a small deposit was found in the side arm S_2, it also was burned off. The valve of the oxygen tank was then closed, P_1 and P_2 opened, the 4 burners turned out, and the asbestos boards and the rubber connections of S_2 and S_4 removed. As soon as the apparatus was almost cool, the rubber stopper, glass wool and boat were removed from H, and then, with the water pump still going, H was flooded with water, rinsing out the apparatus into the absorption train. Finally, the stopper in H was replaced, and the whole apparatus steamed out by boiling off the water remaining in the holder and combustion tube. From this point, the procedure was that already detailed.

In the following tables, when no Carius determinations are given, the materials were considered especially pure, and also time was lacking. Again the results speak for themselves.[1]

TABLE II.[a]

p-Bromo-*o*(β-γ-dibromopropyl) phenylbenzoate, Calc., 50.29% Br.

Combustion.				Carius.		
No.	Sample. G.	Time. Min.	Br. %.	No.	Sample. G.	Br. %.
1	0.2441	95	50.00	3	0.2442	50.10
2	0.2451	60	49.98	4	0.2955	50.02
		Mean,	50.04			50.06

[a] The sample of material for this work was kindly furnished by Mr. V. L. Harnack, who had previously carried out one Carius determination. Having dried his precipitate in a Gooch crucible for one hour at 110°, he obtained a value of 50.23% Br. In all instances, in this investigation, however, the Gooch crucibles were dried at 130° (first empty, and then with precipitates) to constant weight.

TABLE III.[a]

Material.	Properties.	No.	Sample. G.	Time. Min.	Halogen. Found. %.	Calc. %.
p-Bromophenyl-β-bromoallyl ether....................	B. p., 171° at 22 mm.	1	0.3194	130	54.06	...
		2	0.2998	165	54.51	54.76
Hexachlorobenzene..........	M. p., 229°	3	0.2431	80	74.60	...
	B. p., 326°	4	0.2484	75	75.01	74.73
m-Iodobenzoic acid..........	....	5	0.3776	100	51.09	...
		6	0.3706	105	50.98	50.98
m-Chloro-nitrobenzene.......	M. p., 44.4°	7	0.2800	75	22.70	...
	B. p., 235.6°	8	0.3167	70	22.52	22.51
p-Bromoaniline.............	M. p., 66.4° B. p., decomp.	9	0.3198	95	46.47	46.18

[a] The material used in the first two determinations was kindly furnished by Dr. S. G. Powell. By a Carius determination, he found 54.1 and 54.4% Br. The other substances were imported.

In conclusion, it is desired to acknowledge the patience and skill of Mr. Paul Anders, the departmental glass-blower, who made all the glass and quartz apparatus used throughout the investigation.

Summary.

1. A simple, rapid, easily executed, and reliable combustion method for the quantitative determination of chlorine, bromine, or iodine in vola-

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[1] This style of apparatus can of course be used with volatile substances. With the ethylene chloride previously analyzed, the following values were obtained: I, 71.62% Cl; II, 71.58% Cl (cf. Table I).

tile organic substances has been developed. No catalytic agent is used. The material, volatilized with air, is drawn through a heated quartz tube; the combustion products are absorbed in alkaline sodium sulfite solution; the excess of sulfite is oxidized; and the halogen is determined by the Volhard volumetric method.

2. With some modification of the apparatus, and with the partial use of tank oxygen, the method is equally applicable to non-volatile organic materials.

3. The method is a general one for the determination of halogen in organic compounds; and, in our opinion, it yields to none in accuracy of results or in ease and convenience of execution.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE HEAT OF SOLUTION AND THE PARTIAL MOLAL HEAT CONTENT OF THE CONSTITUENTS IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

BY MERLE RANDALL AND CHARLES S. BISSON.

Received November 28, 1919.

In order to calculate the free energy of a reaction at one temperature, when the free energy at another temperature is known, we must first obtain the value of ΔH, the increase in heat content accompanying the reaction.[1] This quantity, is defined as the difference between the heat contents of the substances formed and the heat contents of the substances disappearing. For pure substances, ΔH is identical with the negative of the heat of reaction as ordinarily measured. In case one or more of the substances involved in the reaction occurs in solution, we must use, obviously, not the molal heat content, H, of the pure substance, but the heat content of the substance when in solution at the given concentration. This quantity $\bar{H}$ is the partial molal heat content, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol of the substance is added to it.

It is not possible to determine the absolute value of H or $\bar{H}$ for any substance, for we can measure only the difference ΔH between the heat content of the substances appearing and those disappearing in a reaction. However, when no ambiguity will result, we have found it convenient, at a given temperature, to call the value of ΔH, when a substance is formed from the elements in their standard state at the same temperature, the molal heat content or the partial molal heat content of the substance. It is in this sense that these quantities are generally used in this paper, and when so used will always be symbolized by ΔH. The symbols H

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[1] Lewis, "The Free Energy of Chemical Substances," THIS JOURNAL, 35, 1 (1913).