molecular weight permits the use of large samples, thus reducing the error of weighing; its stability and lack of hygroscopicity make it very convenient, and the method is rapid, since a single weighing and a titration are all the operations involved. These considerations, combined with the ease of obtaining it in a high state of purity, make benzoic acid an excellent material to use as a standard in acidimetry and alkalimetry.

WASHINGTON, D. C., May, 1912,

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE ESTIMATION OF HALOGENS IN ORGANIC COMPOUNDS, INCLUDING A DEVICE FOR THE COMBUSTION OF VOLATIL SUBSTANCES.

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Received June 1, 1912.

In the ordinary combustion methods for the estimation of carbon and hydrogen, it has long been customary, when burning compounds containing halogens, to insert a roll of silver foil to absorb the halogens and so prevent them from reaching the absorption train. This would suggest the absorption of the halogens on weighed silver foil as a possible method for their estimation. However, in the old methods of combustion, in which copper oxide or lead chromate served as sources of oxygen, more or less of the halogen was retained by the copper and lead. Experience[1] with the elegant electrical combustion methods of Morse and his co-workers[2] suggested that the combustion might be carried on without the use of metallic oxidizing agents, and the halogen absorbed by silver.

To test this idea, an experiment was made in which 0.2283 gram of ethyl *p*-bromobenzoate was burned and the halogen absorbed in a boat, 100 mm. long, of silver foil, filled with silver clippings. The gain in weight of the boat was 0.0703 gram, corresponding to 30.8% of halogen out of a calculated 34.9%. The combustion was carried out with great care, taking 1½ hours. The portion of the tube containing the boat was kept at 250°.

A consideration of conditions in the combustion tube shows that the vapors of the substance being burned may be more or less decomposed by the heat before they come into a region in the tube in which there is an excess of oxygen. As is well known, organic halogen compounds give hydrogen halides when decomposed by heat in absence of excess of oxygen, and may give more or less of such halides even in presence of an abundance of oxygen. It is also well known that the complete oxidation of such halides is difficult. Hence provision must be made for the

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[1] *Am. Chem. J.*, **47**, 416.

[2] *Ibid.*, **33**, 590; **35**, 451.

absorption of the hydrogen halides as well as of the free halogens. If the halides can be readily absorbed there will be less need for thorough oxidation and the time taken in the burning may be shortened and the amount of oxygen supplied curtailed. Silver oxide is a most suitable agent for absorbing the hydrogen halides. Then if the decomposition products arising from the more or less incomplete combustion of an organic halogen compound are passed over a mixture of silver and silver oxide, the halogen will be absorbed whether it be present free or in combination with hydrogen.

Since silver oxide melts and decomposes at 300°, the boat containing it must be kept at a temperature below this. On the other hand, since the activity of the silver and halogens is greater and the diffusion of the gases more rapid at elevated temperatures, the silver mixture should be kept at as high a temperature as may be, not to decompose the silver oxide. The most suitable safe temperature would seem to be about 270°. In the analyses given below, the temperatures recorded were from 250 to 293°.

Since during the absorption of the halogen some oxygen is lost, the net gain in weight of the boat during the process will be somewhat less than the weight of the halogen absorbed. However, if the amount of silver oxide originally present is known and the remaining silver oxide reduced before the final weighing, it is easy to calculate the amount of halogen absorbed. Müller[1] has shown that silver oxide is reduced in hydrogen at 85°. About 170° was chosen as a safe and convenient temperature at which to reduce the silver oxide remaining after the combustion. Experiment showed that a boat containing silver halides may be heated in a current of hydrogen at this temperature and even considerably higher, without loss of weight.

These considerations led to the following method for the estimation of halogens in organic compounds.

AO is a tube of transparent quartz, 600 mm. long and 18 mm. bore, supported at *H* and *N*. *B* is a loose plug of asbestos, *C* the silver boat, and *I*, a plug about 75 mm. long of quartz wool. *K* is a second plug of the same material fastened by a piece of fine platinum wire to the 3 mm. quartz tube *JQ*. This tube is 300 mm. long and extends through the two-hole rubber stopper at *O*. *L* is the boat containing the compound to be

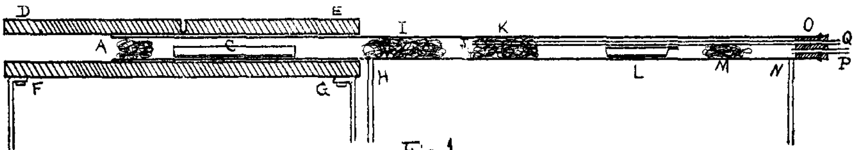

Fig. 1.

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[1] Quoted in Mendeléeff's "Elements of Chemistry."

burned and *M* is a third plug of quartz wool. *P* is a glass tube also passing through the rubber stopper. *DEFG* is a square brass block 50 × 50 × 300 mm. with a 25 mm. hole through its center from end to end. This was adapted from the aluminium block used by Richards, and was found to be very useful for this and for many other purposes. The temperature is given by thermometers stuck in Wood's metal contained in holes drilled in the block. The silver boat, C, is made from a strip of silver foil 25 × 100 mm., bent into a semi-cylindrical trough so as to slip easily into the combustion tube. The ends are turned up about 2 mm. so as to prevent particles of powder from rolling out of the boat. It is best made by shaping the silver foil on a polished metal rod of the proper size and about 4 mm. shorter than the foil. A shield of thick asbestos board is suspended over the tube so as to cover the plug *I* and nearly all of plug *K*. Instead of the brass block an air bath or other heating arrangement might be used, and, doubtless, tubes of hard glass might be made to serve instead of quartz. The high temperatures which may be used with the quartz tubes insure the combustion of the most refractory substances. The rapidity with which quartz tubes may be heated up or cooled down saves much time and aids in regulating the combustion. The long life of a quartz tube under severe conditions makes it economical in the end. The size tube used in this method is also adapted to the estimation of sulfur and to ordinary combustions for carbon and hydrogen. Ordinarily five Bunsen burners are used, one to heat the brass block, one under each of the quartz wool plugs, *I*, *K* and *M*, while one is held in the hand and is used to heat the boat containing the compound, to which heat is applied as required. The two burners under plugs *I* and *J* should give strong flames and are provided with wing-tops.

Silver Oxide.—This is prepared by precipitation from silver nitrate, washed a number of times by decantation, and filtered on a hardened filter. Care should be taken to avoid contamination by dust or fibers from filter paper. It is well dried at 100°, thoroughly mixed, and sealed up in 0.5–1 g. portions. In sealing it up care must be taken not to heat the portion of the tube containing the oxide. The percentage loss in weight is determined for the lot by heating a portion in purified hydrogen to 160–170° for 30 minutes. The preparation used in the present work lost 8.92% on reduction in this way, 0.8623 g. lost 0.0769 g. The calculated amount of oxygen in Ag_2O is 6.90%. Carey Lea[1] has shown that silver oxide retains water at 100° and only parts with it on reduction. The presence of water in it is of no consequence so long as the material is uniform.

Carrying Out a Determination.—The silver boat is cleaned, dried, filled with silver powder, and weighed. The silver powder obtained in deter-

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[1] Quoted in Mendeléeff's "Elements of Chemistry."

mining the loss of weight on reduction of the silver oxide serves for this. When an analysis is finished the silver halide is roughly separated from the slightly affected silver powder and the latter used over again. From 0.2 to 0.5 g. of the silver oxide is sprinkled over this and the whole reweighed. The boat is then put in place and a wad of asbestos placed in the open end of the combustion tube. The end of the combustion tube containing the boat is shoved into the brass block which may be already heated to 270°. The stopper at *O*, with the tube *JQ*, is partially withdrawn and the boat containing the substance to be burned is slid in under the tube *JQ*. Then the plug *M* is inserted and the stopper at *O* pushed in tight. The burners under the plugs *I* and *K* are lit and the asbestos shield placed over the tube. When the central portion of the tube is quite hot, a slow current of oxygen is admitted through the small tube and the burner under the plug *M* is lit. In order to drive the combustible gases through the quartz plug *K*, a slow current of air, or nitrogen, is passed in through the tube *P*. This current must be sufficient to prevent backward diffusion of vapors from the burning substance, but excess is to be avoided as it is desirable to keep the total flow of gases through the tube as low as possible. Air is commonly used, but if an explosion is feared, nitrogen may be substituted.

The combustion is started and regulated by heating the portion of the tube containing the boat. This is done with a burner which is held in the hand. By looking obliquely in under the end of the asbestos shield, the operator can see most of the plug *K*. When the combustion is proceeding just right, from one-third to one-half of this plug is blackened by carbonization of the vapors passing through it while the end toward the plug *I* is kept burned white by the backward diffusion of the oxygen. If more than this much of the plug is blackened, the substance is being volatilized too fast or not enough oxygen is being supplied. After some experience has been gained the combustion may be carried out quite rapidly and with the use of only a small amount of oxygen. From the time the heating of the substance is begun till the tube is burned clean should take about 20 to 30 minutes for the usual 0.2 g. of substance to be burned. If a difficultly combustible residue is left in the boat, oxygen may be admitted at *P* to complete the combustion. The heating and the passage of air and oxygen through the tube are continued for some 5 minutes after the tube has been burned white, to insure the sweeping out of all of the products of combustion, then all the burners are extinguished. When the brass block has cooled to 170°, purified hydrogen is passed for 30 minutes to reduce the remaining silver oxide. The boat is then cooled and weighed. As silver foil, silver oxide, and silver halides are not hygroscopic, it is unnecessary to use a desiccator.

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 Simultaneous Estimation of Carbon, Hydrogen and Halogen.—The same considerations apply to this as to the simultaneous estimation of carbon, hydrogen, and sulphur which has been discussed in a recent article.[1] The difficulty might be overcome by passing the gases that pass the silver boat over a small amount of hot copper oxide to complete the oxidation of the carbon to the dioxide before passing them into the usual absorption train.

The Combustion of Volatil Substances.—The following contrivance has been found to work satisfactorily with volatil liquids. It should serve just as well for ordinary carbon and hydrogen determinations in such substances. In the sketch, Fig. 2, the large tube is the right hand portion of the combustion tube which is set up for the analysis as usual. A piece of hard glass tube about 15 mm. inside diameter is drawn down to about 5 mm. external diameter at about 100 mm. from one end and the 5 mm. portion further reduced to 3 mm. The 5 mm. portion is some 180 mm. long and the 3 mm. part about 250 mm. The tube is bent so as to form a U-tube *UXT*, with the largest portion as one limb. The small portion, *SY*, passes through a T-tube, *R*, and ends at *Y* just where the boat would usually be placed. One end of this T-tube just passed through the stopper in the end of the combustion tube while the other end is joined gas-tight, by a piece of rubber tubing, to the 5 mm. portion of the bent tube. The liquid to be burned is sealed up and weighed in a small bulb which is placed in the larger limb of the U-tube. This is closed by a two-hole rubber stopper which carries a long glass rod, *V*, and a tube, *W*. Air, or nitrogen, is passed in steadily at *R* at a rate sufficient to prevent backward diffusion of the decomposition products. *M* is the same quartz plug as in Fig. 1.

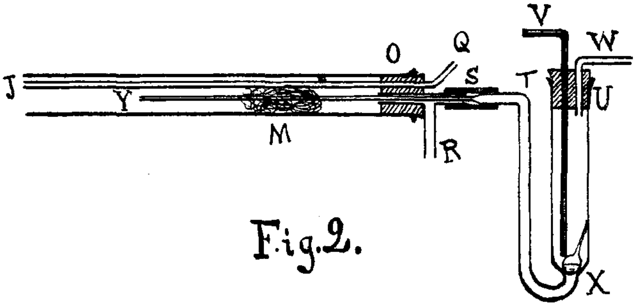

Fig. 2.

When the combustion tube is well heated and all is ready for the burning to begin, the bulb containing the liquid is broken by the rod *V*, while

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[1] *Am. Chem. J.*, 47, 424.

a current of air, or nitrogen, is passed in through the tube *W*, sweeping the vapors of the liquid over into the combustion tube. The rapidity of the combustion is controlled by regulating the current of air admitted at *W* and by varying the temperature at which the U-tube is kept. According to the volatility of the compound to be burned the U-tube is placed in a beaker of hot or cold water or surrounded by a freezing mixture. When no more liquid remains in the U-tube, the bath is removed and the U-tube finally warmed. Methyl bromide, b. p. 4.5°, was burned, by the aid of this contrivance, without the least difficulty. In this case the U-tube was surrounded by ice and salt. This apparatus was used in the analyses of ethyl iodide, which are given below.

Test Analyses.—The 11 analyses below are consecutive and are given in the order in which they were made. They comprise all the determinations that were made except several subsequent analyses of commercial methyl bromide which were rejected as the stopper in the end of the combustion tube was found to be split. The substances chosen include compounds of all three of the halogens, and range in physical properties from *p*-bromobenzoic acid, m. p. 256°, to ethyl iodide, b. p. 72°. As experience was gained with the method, the time of the combustion was cut down. The silver oxide used lost 8.92% on reduction. The "calculated loss" was obtained by taking this percentage of the weight of the oxide used. The "change in weight" of the boat is + or — according to whether the boat gained or lost during the combustion. It is accordingly added to, or subtracted from the figure just above it to obtain the weight of halogen absorbed. The "time" given is the number of minutes from the moment that the heating of the boat was begun till the boat and surrounding tube were burned clean.

The results show that the method gives reliable and sufficiently accurate results. The two analyses, Nos. 8 and 10, which are considerably too low, show strikingly, however, the ability of the silver-silver oxide mixture to absorb halogens. In No. 8 over 0.5 g. of the ethyl iodide was burned in 22 minutes and in that short time the boat actually caught 406.0 mg. of iodine out of a possible 410.3 mg. In No. 10 the absorp-

p-Bromobenzoic Acid, 39.76 Per Cent Br.

Number	1	2	3
Time	39	27	39
Oxygen used, cc.	......	......	......
Weight substance	0.2024	0.2342	0.2157
Weight Ag_2O	0.7887	0.6746	0.7526
Calculated loss	0.0703	0.0602	0.0671
Change in weight	+0.0104	+0.0323	+0.0148
Halogen absorbed	0.0807	0.0925	0.0819
Percentage found	39.87	39.50	39.76

p-Chlorobenzoic Acid, 22.66 Per Cent Cl.

Number	4	5	6	7
Time	28	35	28	20
Oxygen used, cc.	......	750	800	750
Weight substance	0.2033	0.2013	0.2000	0.2027
Weight Ag_2O	0.7631	0.8317	0.3009	0.5893
Calculated loss	0.0681	0.0742	0.0268	0.0526
Change in weight	—0.0219	—0.0289	+0.0181	—0.0071
Halogen absorbed	0.0462	0.0453	0.0449	0.0455
Percentage found	22.72	22.50	22.45	22.45

Ethyl Iodide, 81.38 Per Cent I.

Number	8	9	10	11
Time	22	21	23	40
Oxygen used, cc.	1250	......	400	560
Weight substance	0.5042	0.2458	0.3851	0.2530
Weight Ag_2O	0.2856	0.3041	0.2996	0.1717
Calculated loss	0.0255	0.0271	0.0267	0.0153
Change in weight	+0.3805	+0.1728	+0.2831	+0.1909
Halogen absorbed	0.4060	0.1999	0.3098	0.2062
Percentage found	80.60	81.33	80.45	81.50

tion was 309.5 out of 313.5 mg. in 23 minutes. In these two analyses the amounts of substance burned, 0.5042 g. and 0.3851 g., are much larger than are commonly used in combustions. It appears that it is safe to burn 0.2 to 0.25 g. of substance in 20 minutes, but it is not safe to exceed that rate.

It is suggested that exactly the same apparatus and method might be used for the estimation of sulfur in organic, and even in some inorganic, compounds. In this case the boat would contain lead peroxide instead of the silver-silver oxide mixture and would be kept at a somewhat higher temperature. This would be practically the electrical method of Morse and Gray with the elimination of the electricity.

It is regretted that a change of residence prevented more extensive and varied experiments with the method.

Summary.

It is shown that the halogens may be readily determined by a combustion method in which the halogens are absorbed in a mixture of powdered silver and silver oxide.

A simple and efficient contrivance is described for the combustion of volatil substances.

BALTIMORE, MD.