XV.—*On a New Method of Estimating the Halogens in Volatile Organic Compounds.*

By RICHARD T. PLIMPTON, Ph.D., and E. E. GRAVES.

THE method now almost exclusively adopted for the determination of the halogen elements in organic compounds is that of Carius, which consists, as is well known, in heating the substance to be analysed in a sealed tube with fuming nitric acid and silver nitrate.

This method, although in many respects an excellent one, is open to certain objections. Amongst these are, the risk which attends experiments with pressure tubes, the uncertain period during which the

tube must be heated to ensure complete decomposition, and the semi-molten condition in which the precipitate is often obtained, rendering it difficult to wash out the last traces of silver nitrate. The only other process which has been much used is that of heating the substance to a high temperature, in a combustion tube filled with quicklime, dissolving up the contents of the tube with dilute nitric acid, and precipitating with silver nitrate. But certain compounds, like chlorobenzene, are only with difficulty decomposed by hot lime; further, the operation of dissolving so large a quantity of lime is objectionable, and either for these reasons, or because of the necessity of using lime free from chlorine, which is not always at hand, the method has fallen into disuse.

J. Volhardt (*Annalen*, **190**, 40) describes a method which has been worked out by Feez, Schraube, and Burekhardt, in which the substance is burnt in a covered porcelain crucible, with a mixture of sodium carbonate and potassium nitrate, or, if a more volatile compound, with the same mixture in a tube. No analyses of very-volatile compounds were, however, made. According to Schiff (*Annalen*, **195**, 293) a very similar process was recommended long ago by Piria, who used two platinum crucibles, the smaller of which, after receiving the substance to be analysed, was filled up with black flux, inverted, and placed within the larger, the ring-shaped space between the two crucibles being then filled with the same compound. Schiff, who substituted for the black flux sodium carbonate, or a mixture of the same with lime, obtained excellent results with solid bodies, and even with some liquids; certain other liquids, however, always partially escaped decomposition.

In the method now to be described, we have used an entirely different means of decomposing the organic substance, namely, by introducing it in the state of vapour into the flame of a Bunsen burner, where the halogens are obtained chiefly in combination with hydrogen, and in small quantity in the free state. The products of combustion are drawn through suitable absorbers containing sodium hydrate, and the halogens so collected are then estimated in the usual way.

After many trials we adopted the form of apparatus shown on p. 121. It consists of a burner (A), easily made from a hard glass bulb tube, and bent as shown in the figure. At B there is the usual Bunsen arrangement for mingling gas and air, and the jet and air-holes are of such a size that with the full pressure of gas, a flame of about three-quarters of an inch in length is obtained. The external diameter of the tube is about $\frac{7}{16}$ inch, and it is contracted at the orifice to $\frac{1}{4}$ inch.

The flame is placed within the conical tube (D), by which the products of combustion are conveyed to the scrubbers (S) (S). Diameter

of tube at widest part, $1\frac{5}{8}$ inch, tapering in 4 inches to $\frac{3}{4}$ inch; length of tube from junction with the scrubber to top of bend, 6 inches.

The scrubbers consist of two **U**-tubes of the form shown, fitted with draining tubes closed by clips, and filled with glass beads. The beads used were in the form of $\frac{1}{8}$ -inch lengths of quill tubing, and were easy to wash. A few large round beads were placed at the top, to keep the others in place. The tube (D) is fitted into the scrubber by means of a ring of india-rubber, and the corks are of the same substance. The dimensions of the **U**-tubes are: diameter of tube, 1 inch; length of short limb, 10 inches; length of inclined tube, 4 inches; width across, 4 inches.

K is a small bottle containing solution of silver nitrate, and serves to indicate the completeness of the absorption, and the rate of the current. It is connected with a Sprengel pump (water). A small weighing tube is required, of such a size that it will easily slide down the burner into the bulb. It must be stoppered, but not contracted at the mouth, otherwise its contents will not readily flow out into the bulb.

The mode of conducting an experiment is the following: the scrubbers are charged with 50 c.c. each of a solution of pure caustic soda, prepared by dissolving 1.5 grams of sodium in 100 c.c. of water, and a current of air is drawn through the apparatus, just sufficient to allow of the Bunsen flame burning steadily within the conical tube. A disc of card may be placed round the burner, so as nearly to close the mouth of the cone, to neutralise the effects of draughts. The liquid to be analysed is then weighed out in the small stoppered tube (0.1—0.25 gram), and the gas having been previously turned on for some seconds, the weighing tube is quickly unstoppered, and dropped down the burner, the gas instantly lit, and the flame placed within the cone. If the liquid has not already run out into the bulb, it is made

to do so, and its evaporation is then aided by warming the bulb with hot water, or otherwise. The temperature of the bulb is raised or lowered, so that the presence of the substance may always be detected in the flame, and yet not in sufficient quantity to cause the flame to become luminous. With some bodies the flame is tinged green; with others, *e.g.*, amyl chloride, a slight luminosity at the tip of the flame is all that is perceptible. The success of the experiment depends upon the regular volatilisation of the compound; on the one hand this must not be unduly hurried, or the flame becomes luminous, and the combustion may be incomplete; on the other, the evaporation should not be too slow, or, before it is complete, the soda in the absorbers will have become carbonated, and therefore incapable of stopping every trace of the free halogen and their acids. The silver nitrate solution will of course indicate when this point has been reached.

Usually the combustion occupies 15–20 minutes, and the silver solution remains clear. As soon as the liquid has disappeared from the bulb and tube, the former is warmed gently with a Bunsen burner, and then more strongly, so as to drive off the last traces.

We have found that the easiest way of securing a slow and regular evaporation in the case of liquids boiling below 100°C ., is to place the stoppered weighing tube *with* its stopper within the bulb; on warming with hot water, sufficient vapour escapes round the stopper. This plan was adopted with good results in experiments made with carbon tetrachloride, 76° ; ethyl iodide, 71° ; ethyl bromide, 39° ; and ethylene chloride, 82° . In the case of ethyl iodide, indeed, it is impossible to use an open tube, for the iodide is so little inflammable and so volatile that the gases refuse to burn at all.

Liquids with boiling points between 100° and 135° are weighed out in a tube from which the stopper is removed on dropping it into the burner. The most convenient way of heating the bulb is to surround it with water kept hot by a current of steam.

With liquids boiling above 135° cautious heating with a Bunsen may be resorted to; the flame must be kept moving, and taken away directly the substance shows its presence in the flame. When the combustion is at an end, the soda-solution is run out from the **U**-tubes into a flask of about a litre capacity, and the wash-water from the same, together with the rinsings of the corks and connecting tubes, added. Generally the total quantity of liquid amounts to about half a litre. Some sulphurous acid is now added, and the contents of the flask boiled down for 10 minutes or more over a large Bunsen, so as to reduce any chlorates, &c., that may have been formed. Nitric acid is then added, the solution precipitated with silver nitrate, and the estimation finished in the usual way. The precipitate may easily be washed from the flask on to the filter.

The following are some of the results obtained by the above method :—

Substance.	Boiling point.	Found.	Calculated.
Ethyl bromide	39°	73·28	73·4
„ iodide	71	81·36	81·41
„ „	„	81·5	81·41
Carbon tetrachloride	77	92·25	92·2
Ethylene chloride.....	82	71·46	71·7
„ „	„	71·4	71·7
Amyl chloride	100	33·29	33·33
Ethylene bromide.....	131	85·17	85·1
„ chloriodide	141	85·2	85·3
Acetylene bromiodide	150	88·78	88·8

Three analyses of an impure specimen of benzal chloride yielded, 43·3, 43·6, 43·3 per cent. chlorine ; a determination by Carius' method gave 43·6 per cent. The above experiments, made with compounds of very various composition and boiling points, will suffice to show that the method described is capable of yielding accurate results. The time occupied by a complete estimation is about two and a half hours.

The experiments here described were made in the Laboratory of University College, London.