

AN ABSTRACT OF THE THESIS OF

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A study of the wet combustion of organic halides by H_2SO_4 and $K_2Cr_2O_7$ was made in order to determine the applicability of KI solutions as absorbents for the liberated halogen.

It was shown by the use of KI solutions as absorbents, in both the wet and dry combustions, that the procedure and the apparatus was simplified.

A number of unsuccessful attempts were made to devise a method for the separation of the oxides nitrogen from bromine. Had these attempts been successful, it would have been possible to adapt the iodometric procedure to all types of compounds.

A MICRO IODOMETRIC METHOD
FOR THE DETERMINATION OF
HALOGENS

by

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INTRODUCTION

The problem of determining halogens in organic compounds has been approached in several ways (2, 6, 7, 11, 12), either by wet or dry combustions or by bomb procedures.

These procedures vary only in the method utilized to liberate the halogen, which is then determined by methods based on gravimetric and volumetric procedures. The wet combustion methods are characterized by the use of liquids and liquid mixtures as oxidants. Dichromates (16) and permanganates (1, 13) in sulfuric acid medium have been most commonly employed in this connection; nitric acid (2, 7, 11, 12) under pressure has also received considerable attention.

The dry combustion methods in use are all based on the principle of catalytic oxidation (11, 12). In these methods the substance is burned in a stream of oxygen and the gases passed over heated platinum foil, in order to insure complete combustion of the compound.

The bomb methods (6) consist in the decomposition of the compound by suitable oxidizing agents in a micro-bomb. This serves as a rapid method of bringing about complete oxidation of the organic halide.

In the wet and dry combustion processes, the halide is converted to free halogen and is then determined by the various volumetric and gravimetric procedures. In the case of the bomb procedure the halogen sometimes reacts with the oxidants and is not freed as in the other methods. This entails certain modifications to liberate the halogen.

In the gravimetric procedures the halogen is usually recovered from the absorption medium as the silver halide. Although this method is accurate, it has all of the limitations associated with gravimetric processes.

Several volumetric methods (9, 16, 17) for the determination of halogen are described in the literature. In some cases, standard base has been used as the absorbent. Zacherl and Krainick (17) have published a method based on the use of this reagent. The hypohalites are reduced with peroxide solution, and the excess base titrated with standard acid. From this data, the amount of the halogen in the sample can be easily calculated.

A modification of this method for iodine determination is described by T. Liepert (9). In the Liepert process the iodide is oxidized to iodate by the use of bromine. The excess bromine is destroyed with formic acid and the iodic acid determined in the usual way with KI and thiosulfate.

Willard and Thompson (16) have recently perfected a method using arsenite solution for the absorption of the halogen. The halogen is determined as the silver halide.

One of the best absorbents for free halogens is KI solution. It is very difficult to aerate iodine from concentrated KI_3 solutions. In this laboratory it was found that KI_3 solutions would retain their iodine even when subjected to vacuum. Since the KI solution has excellent retaining and scrubbing properties, it was the opinion of the authors that it might serve as an excellent absorbing agent for the determination of halogens, as well as simplifying existing procedures. For this reason the present investigation was undertaken.

Most of the methods described in the literature require special apparatus, and in many cases it is of complicated design. From the initial experiments, it was evident to the authors that the use of KI solutions as the absorbing medium would greatly simplify the apparatus.

METHOD

Apparatus--

The wet combustion apparatus of Pyrex glass is illustrated diagrammatically in Fig. 1. The reaction vessel A (volume 6 ml. to the ground glass joint) was

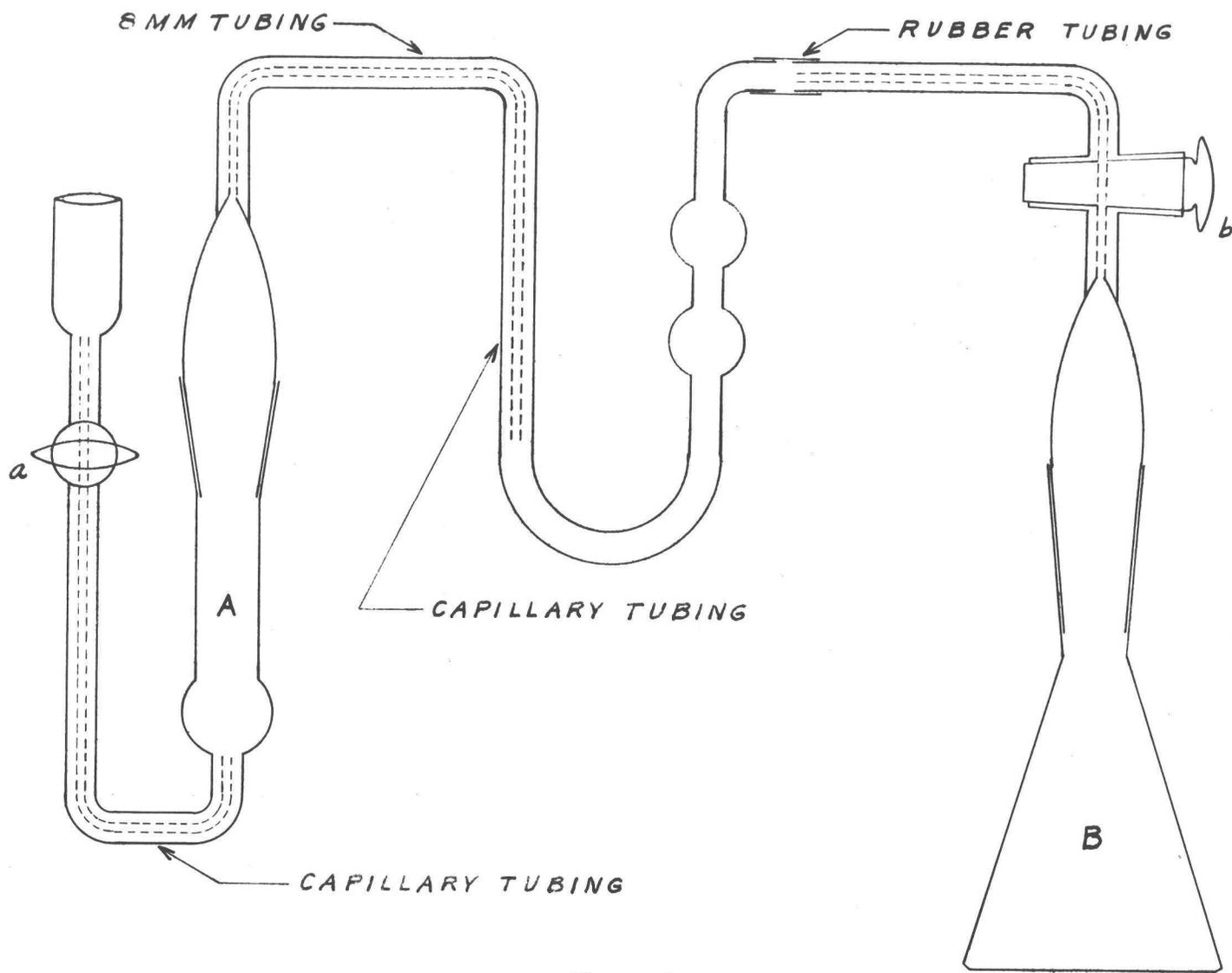


FIG. 1

constructed from a No. 11 standard taper joint and a capillary stopcock a. Part of the U tube, as shown in the diagram, is constructed of capillary tubing, the rest of 8 mm. tubing. The flask B was constructed of a 250 ml. Erlenmeyer flask, a No. 20 standard taper joint, and capillary stopcock b. This served as a convenient source of vacuum during the aeration of the reaction vessel.

The heating bath was made from a 250 ml. beaker, wound with fifteen turns of No. 22 nichrome wire. The temperature was controlled by two tubular rheostats (A = 22 ohms, B = 20 ohms) in series acting as a potential divider, Fig. 3. Phosphoric acid 85% (3) was used as the bath medium. This arrangement permitted the control of the temperature within 5° C. with only an occasional readjustment.

The boats used in the wet combustion were made from Pyrex glass and had the following dimensions: depth, 4 mm.; length, 9 mm.; width, 5 mm.

The dry combustion boats were of platinum and of the following dimensions: length, 11 mm.; width, 4 mm.; depth, 4 mm.

The dry combustion apparatus, Fig. 2, consists of a 45 cm. quartz tube of 8 mm. internal diameter. The catalyst consists of three pieces of platinum foil, rolled to a diameter of 7.5 mm., or just slightly smaller than the tube. The absorption apparatus consists of a 6-inch Pyrex

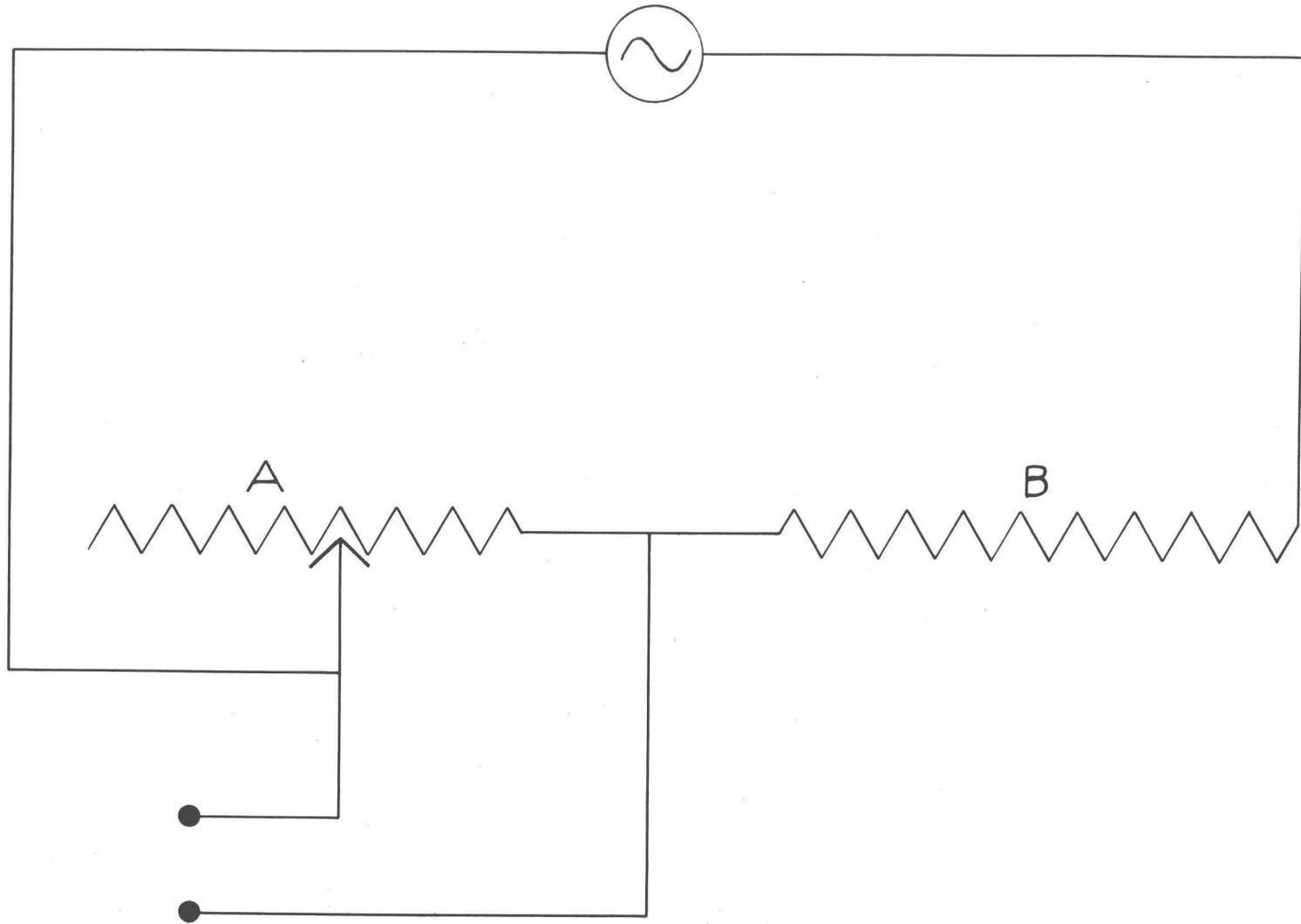


FIG. 3

test tube fitted with a two-hole rubber stopper. The gases from the combustion are led by means of a tube through the KI solution. From the test tube the gases pass through a U tube to insure complete removal of the halogen from the gas stream.

Solutions and Reagents--

1. Sodium Thiosulfate. An approximately 0.005 N solution was prepared by dissolving 1.58 grams of the anhydrous salt in two liters of distilled water containing 2% of amyl alcohol for stabilization and standardized against KIO_3 .

2. Starch solution. The starch solution was prepared by triturating 0.2 grams of soluble starch with a small amount of water, adding it to 100 ml. of boiling water and filtering.

3. Potassium Iodide. The C.P. salt was found to contain only small amounts of KIO_3 , thus giving negligible blank values.

4. Potassium Iodide solution. This was 10% KI and contained 1% BaCl_2 .

5. Potassium Dichromate. A.C.S. standard.

6. Sulfuric Acid. The C.P. A.C.S. grade was used.

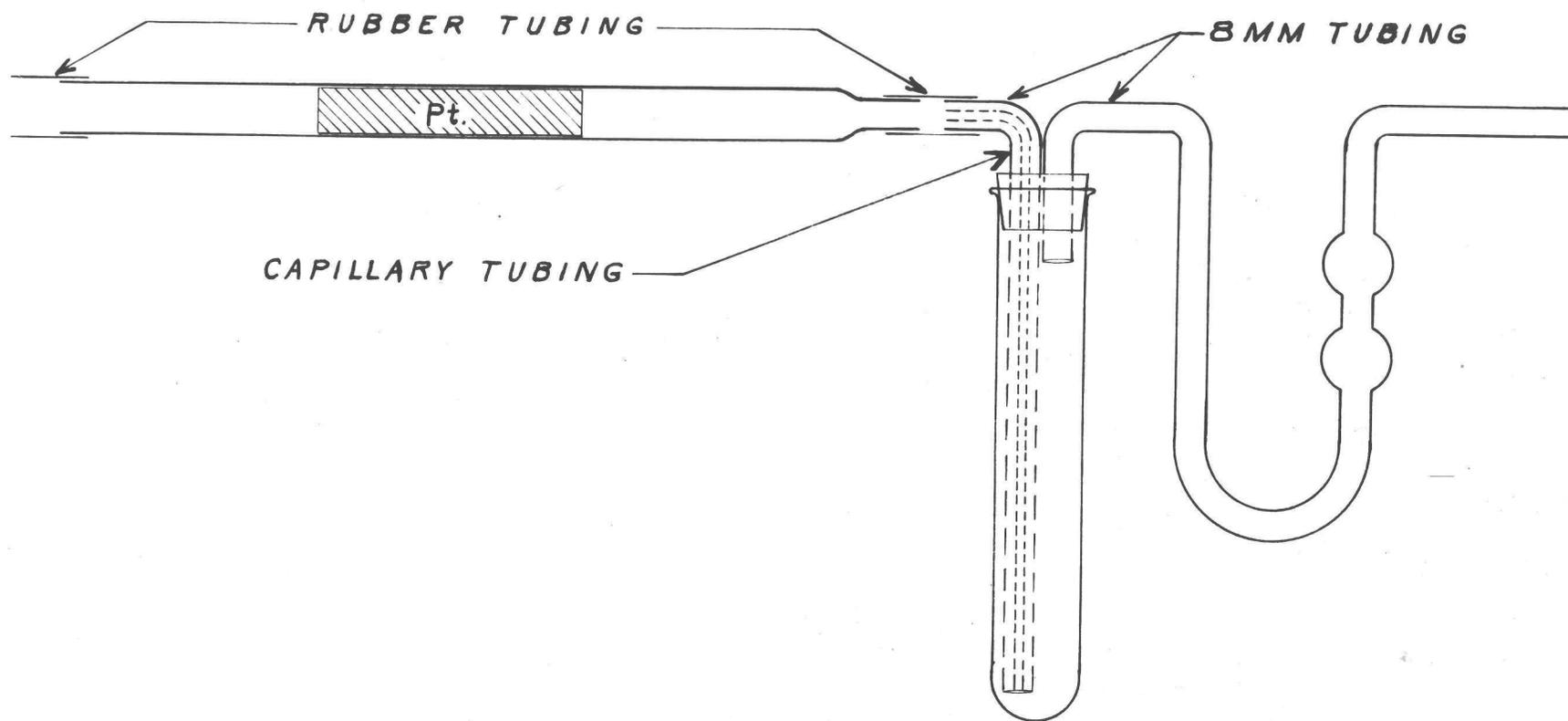


FIG. 2

PROCEDURE

Wet Combustion--

Samples of 2-6 mg. of organic material were weighed in a glass boat to the nearest three micrograms by means of the microchemical balance. The boat was then introduced into the reaction vessel along with approximately 100 mg. of $K_2Cr_2O_7$. One ml. of the KI solution was placed in the U tube, the male joint then lubricated with syrupy phosphoric acid and the unit assembled.

One ml. of the concentrated sulfuric acid was then allowed to flow through the capillary stopcock into the reaction vessel. The stopcock was closed and the vessel immersed in a phosphoric acid bath, which is maintained at $190 \pm 5^\circ C.$, for from thirty to sixty minutes, depending on the nature of the compound undergoing oxidation. The gases which were generated were forced through the U tube by the internal pressure of the vessel. At the completion of the heating period, the evacuated flask was attached to the system and a current of air slowly drawn through the apparatus for ten to fifteen minutes. This insures complete removal of the halogen from the reaction vessel.

The KI_3 solution was then washed out of the U tube into a 125 ml. Erlenmeyer flask, diluted to 10 ml. with distilled water and titrated with 0.005 N thiosulfate

solution.

Dry Combustion--

Two to six mg. of the organic compound to be analyzed was weighed into a platinum microboat.

The combustion tube and absorption train was assembled as shown in Fig. 2. Five ml. of the KI solution was placed in the test tube and one ml. in the U tube. The absorption train was attached to the combustion tube by means of a short piece of rubber tubing.

The sample was then placed in the ignition tube and a stream of oxygen flowing at the rate of sixty bubbles per minute was admitted. The platinum foil catalyst was heated by means of two Meeker burners. The sample was then slowly burned with a Bunsen burner by gradually advancing toward the substance, heating directly under it for about ten minutes, and then moving the flame up to the burners that heat the platinum catalyst. After completion of the combustion the burners are turned off and the oxygen allowed to sweep out the tube for about twenty minutes.

The KI_3 solution was then washed out of both the test tube and U tube into a 125 ml. Erlenmeyer flask and titrated with 0.005 N thiosulfate solution.

DISCUSSION AND RESULTS

The results obtained for the dry combustion processes are tabulated in Table 1.

Table 1

<u>Compound</u>	<u>Per Cent Halogen</u> <u>Theoretical</u>	<u>Actual</u>
Dibrom-p-dimethoxybenzene	54.0	53.8 53.9 53.9 54.1
* p- Bromphenyl Benzoate	28.8	27.9 28.0 28.5 28.1

* This compound was shown by other methods to be impure and to contain 28.0% bromine.

The results from the wet combustion processes are tabulated in Table 2.

Table 2

<u>Compound</u>	<u>Per Cent Halogen</u> <u>Theoretical</u>	<u>Actual</u>
p-Bromacetanalide	37.3	37.3 37.1 37.5 37.2
Tetramethyl Ammonium Bromide	51.9	51.6 51.5 51.5 51.7

Table 2 (Cont.)

<u>Compound</u>	<u>Per Cent Halogen Theoretical</u>	<u>Actual</u>
p- Phenylphenacyl Bromide	29.1	28.9 29.0 29.1 29.4
Dibrom-p-dimethoxybenzene	54.0	54.1 53.9 53.8 53.9
* p-Bromphenyl Benzoate	28.8	28.0 28.0 27.9 27.9
Diphenyl Carbylamine Chloride	22.9	13.9 14.6 14.0 14.5
Chloral Hydrate	64.3	56.1 52.9 36.5
o- Iodobenzoic Acid	51.2	4.90 7.70
Semicarbazide Hydrochloride	32.7	27.6 30.0 32.9 28.9
Triphenylchlormethane	26.4	10.1 7.58 8.92 9.34

* This compound was shown by other methods to be impure and to contain 28.0% bromine.

Although a great deal of attention has been given in the literature to wet combustion processes (2, 7, 11, 12, 17) involving halogens, it is the opinion of the authors that they lend themselves to the determination of only a limited number of compounds.

It is the writers' opinion that any organic substance may be quantitatively oxidized by wet combustion providing the material can be retained in the oxidizing medium. However, it appears from the results submitted in Table 2 that the compounds that are soluble in H_2SO_4 are most easily analyzed. It is the authors' conviction, based on experience, that solubility is the dominant factor in wet combustion processes, with specificity of oxidation and volatility also playing important roles.

Many of the organic halogen compounds are both insoluble in H_2SO_4 and volatilize at low temperatures. These compounds give erratic results.

Iodine compounds (9, 10), because of the difficulty of quantitatively removing the free iodine from the reaction medium, are not satisfactorily treated by wet combustion methods.

In the treatment of halogen compounds containing reduced nitrogen, wet combustion methods are very satisfactory. In these cases the nitrogen is retained as the ammonium salt, while the halogen is readily carried away in the gas stream. At present this method is the only

one available by which halogen can be determined in the presence of nitrogen by a volumetric method.

The wet combustion method is not effective in the case of compounds containing oxidized nitrogen, because the NO_2 released oxidizes the KI. In the case of dry combustions with compounds containing nitrogen, the NO_2 formed interferes in the same way.

A great deal of time was spent during this investigation in an attempt to develop a method in which the formation of the nitrogen oxides would not interfere.

Experiments were conducted in which the halogen was absorbed in NaOH, and the hypohalites reduced with urea. A known amount of KIO_3 was added and the solution acidified. The bromide was transformed into the free halogen and removed by aeration. This method was abandoned because small amounts of iodine were also carried over, rendering the method impracticable.

The use of bromates as the oxidizing agent was also tried but abandoned because of the decomposition of the bromate in solutions of the acidity needed for the release of the halogen.

A KIO_3 solution was used, the thiosulfate titer of which was known. In this the halogen was reacted in H_2SO_4 solution with 2 cc. of the KIO_3 , and the halogen

formed removed by steaming. The excess KIO_3 was determined with KI and thiosulfate. From the difference in titer the halogen was calculated. This, probably because of high dilutions, gave erratic results.

Absorption experiments were also attempted. It was thought that the NO_2 might be absorbed by pumice saturated with $\text{H}_2\text{SO}_4(4)$. This gave low and erratic results due to the absorption of some of the bromine as well as the NO_2 . Attempts were also made to absorb the NO_2 in solutions of urea and of ammonium chloride. These gave negative results.

An attempt was also made to oxidize the halide to bromate and determine it iodometrically. This entailed the use of chlorine as the oxidant. The results showed promise but would require much work before they could be perfected.

SUMMARY

1. The applicability of KI solutions as an absorbent for halogens has been demonstrated.
2. Both the wet and dry combustion apparatus have been materially simplified.
3. Studies of wet combustion of organic halogens have been carried out.
4. Unsuccessful attempts have been made to devise a method for the separation of the oxides of nitrogen from bromine. Thus, this would adapt the volumetric procedure to all types of combustions.

BIBLIOGRAPHY

1. Buchholz, J. J. Arch. exptl. Path. Pharmakol. 81, 289 (1919).
2. Carius, L. and Houben, J. "Die Methoden der organischen Chemie." G. Thieme, Leipzig, 1925, Vol. 1, pp. 59-63.
3. Christensen and King. Ind. Eng. Chem. Anal. Ed. 8, 194 (1936).
4. Dennis, L. M. "Gas Analysis." The Macmillan Company. New York, 1913, p. 223.
5. Dennstedt, M. "Anleitung zur vereinfachten Elementaranalyse." V. Meisner's Verlag, Hamburg, 1919.
6. Elek, A. and Co-workers. Ind. Eng. Chem. Anal. Ed. 9, 502 (1937). J. Am. Chem. Soc. 55, 2550, 3479 (1933).
7. Emich, F. and Donau, J. Monatsh. 30, 745 (1909).
8. Kimball, R. H., Wittenberg, H. H., Mac Fayden, D. E. Ind. Eng. Chem. Anal. Ed. 9, 48 (1937).
9. Leipert, T. Mikrochemie, Pregl Festschrift, 1929, p. 266.
10. Lunde, G. and Gloss, K. Mikrochemie, Pregl Festschrift, 1929, p. 272.
11. Pregl, F. "Die quantitative organische Mikroanalyse." Third Ed., J. Springer, Berlin, 1930, pp. 131-151 and pp. 179-180.
12. Roth, H. and Daw, E. B. "Quantitative Organic Microanalysis of Fritz Pregl." P. Balkiston's Son and Co., Inc., Philadelphia, P. A., 1937, pp. 94-116.
13. Sanchez, J. A. Mikrochemie, 10, 194 (1931).

14. Vieböck, F. Ber. 65, 393 (1932).
15. Vieböck, F. and Brecher, C. Ber. 63, 3207 (1930).
16. Willard, H. H. and Thompson, J. J. J. Am. Chem. Soc. 52, 1893 (1930).
17. Zacherl, M. K. and Krainick, H. G. Mikrochemie 11, 61 (1932).