

THE USE OF LIQUID AMMONIA AS A SOL-
VENT IN A METHOD FOR THE QUANTITATIVE DE-
TERMINATION OF THE HALIDES IN ORGANIC COM-
POUNDS.

By

Howard N. Calderwood, Jr.

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THE USE OF LIQUID AMMONIA AS A SOLVENT IN A METHOD FOR THE QUANTITATIVE DETERMINATION OF THE HALIDES IN ORGANIC COMPOUNDS.

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Historical.

Of the various methods for the quantitative determination of the halogens in organic compounds, the wet method of Carius and the three ignition methods are the only ones applicable to all classes of compounds.

The ignition methods¹ are three in number, namely: the lime, the ferric oxid, and the brown copper oxid methods, all of which require from four to eight hours and the combustion furnace with its many accessories.

The wet method of Carius⁽¹⁾, which is the method most generally used, requires heating the substance from one and one-half to three hours in a bomb furnace, and is accompanied with the danger of explosions and the ever present liabilities of such.

The alcohol and metallic sodium or potassium method of Stepanoff⁽²⁾ and its modifications⁽³⁾ are applicable to only a limited number of substances, and also the operation requires considerable time and

(1) Fresenius: "Quantitative Analysis", vol. II, pp. 121-128, 1904.

(2) Ber., vol. 39, p. 4056, 1904.

(3) Bacon: J. Am. Chem. Soc., vol. 31, p. 49, 1909. Maryett: Am. J. Sci., vol. 30 (14), p. 378, 1910.

care.

Comparison of the Methods.

The ignition methods are very difficult to operate because considerable care must be used to keep any of the halide from escaping, either undecomposed or after it is liberated. Then also, after the decomposition is finished, a large mass of material must be removed from the combustion tube, and there is a considerable quantity that can be removed from the inner walls of the tube only with difficulty.

The method of Carius is one where the time necessary for the decomposition must be determined for the different substances studied. Then the danger from explosion is considerable at the time of sealing the bomb tube, and if the tube is not carefully heated, the entire determination may be lost because of the destruction of the tube. Care must also be used in removing the residues containing the silver salt of the halide. The alcohol method of Stepanoff is not capable of application to the more complex halide compounds, and reacts only with difficulty upon the benzene derivatives.

Proposed Method.

Some twelve or fifteen years ago, Dr. H. P. Cady, of this laboratory, while carrying on some studies in liquid ammonia, found that aliphatic organic halides were quantitatively reduced by metallic sodium when dissolved in anhydrous liquid ammonia⁽⁴⁾. Dr. Cady, while investigating this reaction, had some difficulty in carrying out the action with the cyclic carbon compounds, and it was the purpose of my research to see if it were possible to reduce the benzene and other cyclic compounds quantitatively by the method outlined.

Knowing that a great many of the organic halides and also metallic sodium and potassium are soluble in liquid ammonia⁽⁵⁾, and also that ammonium salts in liquid ammonia are analogous to their respective acids in water, it was planned to reduce the halides with an excess of metallic sodium, using liquid ammonia as the solvent. The excess of sodium was then

(4). Not published.

(5). Franklin and Kraus: Am. Chem. J., vol. 20, p. 828, 1898.

to be removed with ammonium nitrate, which, in the ammonia system of acids, bases and salts, corresponds to nitric acid in the water system⁽⁶⁾. The solvent would then be allowed to evaporate, the residue dissolved in water and the halide determined by the titration method of Volhard:

The reagents required for this work are: Commercial liquid ammonia, metallic sodium, ammonium nitrate, standard solutions of silver nitrate and potassium sulfocyanate, a ten per cent solution of nitric acid, and a saturated solution of ferric ammonium sulfate. The sodium, ammonium nitrate and ferric ammonium sulfate must be free from substances that will precipitate silver. The nitric acid solution should be free from oxides of nitrogen, and the solution of ferric ammonium sulfate must be a clear filtered solution.

The standard solutions of silver nitrate and potassium sulfocyanate were made approximately tenth normal and then filtered through separate washed and ignited asbestos filters. These two solutions were then standardized by using recrystallized chemically pure so-

(6) Franklin: J. Am. Chem. Soc., vol. 27 (1), p. 820, 1905.

dium chloride, potassium bromide and potassium iodide, using the same method as was later followed in the investigations.

The apparatus used outside of that in common use in quantitative analyses were the Dewar tubes for holding the liquid ammonia, and the arrangement of the connections for obtaining the liquid ammonia from the tank. See Fig. 1. The Dewar tubes (B), after being fitted tightly to the rubber stopper, were clamped to keep them from being blown off in case the pressure upon opening the valve (D) became excessive. The ammonia vapors were absorbed by passing from the tube (B) through the lines (c and d). Each of these lines was fitted with a series of three large bottles filled two-thirds full of distilled water and arranged as in an ordinary gas washing system. All stoppers used in this work must be rubber, and all stopcocks must be carefully ground and well oiled to prevent leaks.

After the Dewar tube was in place and fastened, the valve (D) was opened slightly and the ammonia vapors were allowed to flow through the entire apparatus, the cocks (a and b) being opened before the valve (D). After the ammonia began to appear as a li-

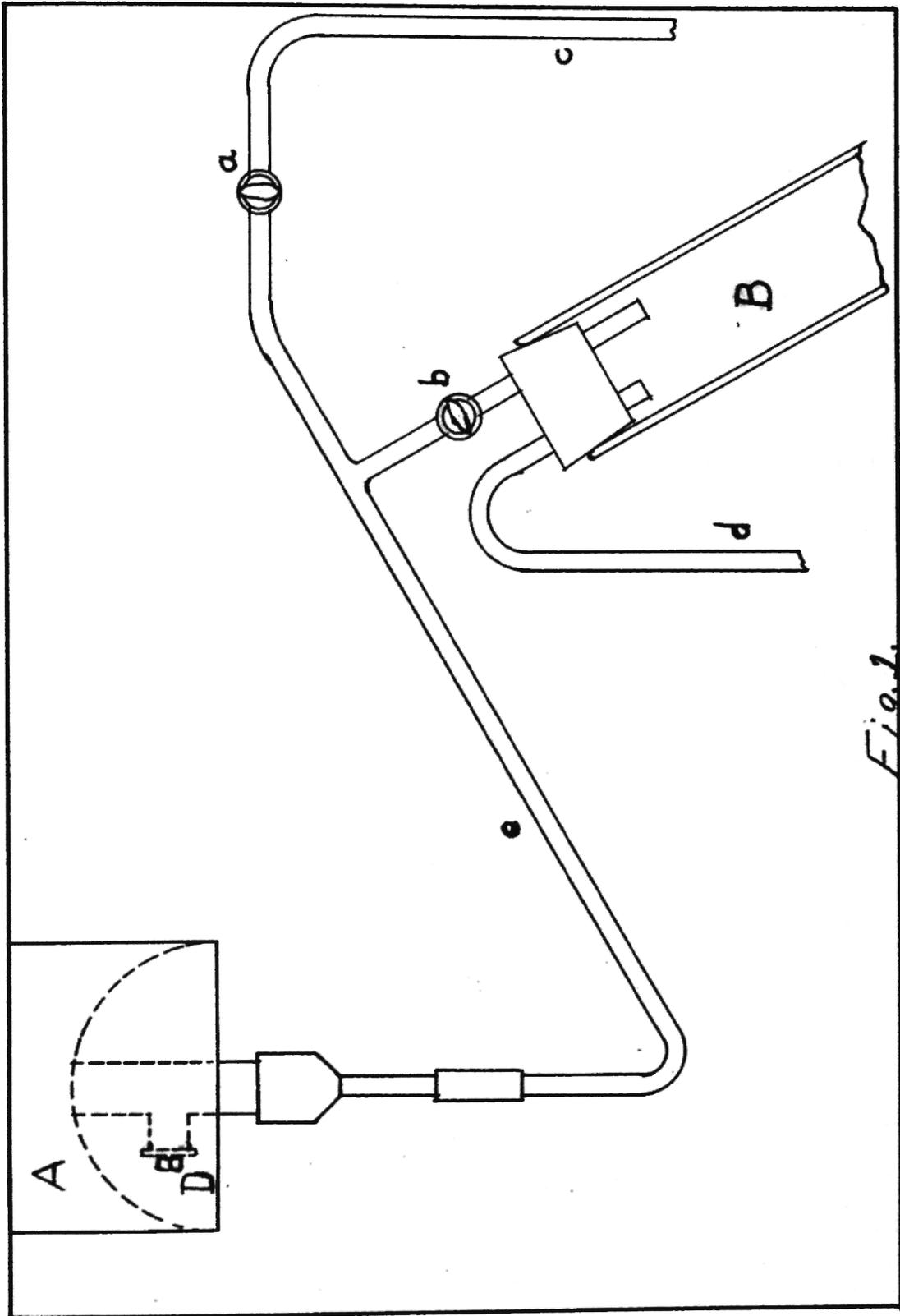


Fig. 1.

liquid in the tube (e), the cock (a) was closed and the valve (D) opened a little more. The liquid ammonia was then allowed to collect in (B) until the tube was full or until all the ammonia needed had been drawn out. In this work, enough determinations were started at one time to require from 100 to 200 cc., of liquid ammonia, to avoid waste due to cooling the apparatus. The ammonia, after being collected in the Dewar tube on the apparatus, was transferred to a silvered one to avoid waste by evaporation. A clear tube was always used for collecting, so as to be able to tell when it was filled. After a tube of ammonia was drawn off, the cock (a) was opened before the cock (b) was closed, and the tube removed and replaced by an empty one. When all of the ammonia desired was obtained, the valve (D) was closed and then the cock (a) opened and the cock (b) closed, in the order named. At no time can the system below (D) be closed completely, because of the danger of an explosion due to the expansion of the liquid ammonia upon warming and vaporizing. In transferring the liquid ammonia to the silvered tube, a small quantity is first poured in from a pipette to cool the tube and to avoid the spattering produced when the large quantity is added.

Before any liquid ammonia was removed from the holder, the amounts of the substances to be studied were weighed into clear Dewar tubes with a capacity of about 100 cc. In the case of solid substances, they were transferred to the tubes direct from the weighing bottles and the difference between the two weights taken. Enough was usually taken to be equivalent to about 15 cc., of silver nitrate. When liquid substances were used, at first they were taken from small Ostwald pyknometers and the difference in weight taken. This method, however, gave so many errors that no satisfactory results could be obtained. Then thin walled bulbs were blown which had very small and thin capillary necks. These were weighed and then filled with the substances by heating the bulb gently with a Bunsen flame to expel the air, the tip being immersed in the substance desired. When allowed to cool, the liquid was drawn into the bulb, and when cold, the capillary was sealed by holding the tip in a flame. The bulbs were again weighed and then put into the Dewar tubes, care being taken not to break them. These bulbs had to have thin enough walls to be easily crushed with a stirring rod by pressing on the bottom of the Dewar tube. The capillary must also be fragile enough to

be broken in this manner to small bits, without danger of breaking the Dewar tube. The bulbs must not be broken until there is enough liquid ammonia in the Dewar tube to cover them in case they should float.

After the bulbs were crushed, the substances were allowed to dissolve, in case the substance had solidified at the low temperature of the liquid ammonia. When the solution was complete, or a saturated solution was obtained, the metallic sodium was added in small quantities and allowed to react completely before any more was added. In case all of the substance was not dissolved at first, it would easily do so when treated with the sodium. The surface of the sodium must be freshly cut and kept as free from oil as possible in order to hasten the reaction. The halides of chlorine and bromine, when acted upon by sodium, usually gave, when the sodium was not present to an excess, a colorless or slightly yellow colored solution, but all iodides, when treated with a little sodium gave a violet colored solution of the same color as fumes of iodine. When the sodium was present in an excess, the solution became an intense blue color and was opaque to light. This color generally would appear before the reaction had reached completion, but upon standing it would grad-

ually change to a brown color. However, when the reaction was complete, the color of the solution would remain blue as long as there was any liquid ammonia in the tube. The solution would become viscous unless a very large quantity of liquid ammonia was present.

When the blue solution was treated with ammonium nitrate, it became mobile and transparent.

There should be no oily particles noticeable if the reaction is complete. At first the ammonium nitrate was added in the solid state, but the action was so vigorous that there was danger of spoiling the determination by loss, due to spattering. Later the ammonium nitrate was dissolved in liquid ammonia to a concentrated solution, and this solution added by means of a pipette. It was found that, if the ammonium nitrate solution was made up in a clear Dewar tube, it soon evaporated, so silvered tubes were used. In adding the ammonium nitrate solution, care had to be used, because if any struck the dry products of the sodium reaction, caused by the evaporation of the liquid ammonia, light would be produced by the heat evolved. As stirring rods were used in all determinations, the ammonium nitrate was allowed to flow down the rod. In one case, before using the rods, the heat produced was so great

that it caused one of the Dewar tubes to crack, thereby producing an explosion which demolished the tube. After the accident, the stirring rods were always used. It was also found advisable to rinse the substances from the sides of the tubes and from the stirring rods with a little liquid ammonia, before adding the ammonium nitrate solution. When the ammonium nitrate solution reacted with the ammonia solution, considerable boiling was produced, but there was never any light produced. The colors of the solutions of the various halides after treatment differed, and will be given under the data for each one. After the evaporation of the ammonia, the residue was dissolved in water and the silver nitrate added, the solution was then filtered, and the filtrate titrated for the excess of silver nitrate.

The time necessary for these determinations, after the weighing was finished, was from thirty minutes to an hour for the reducing action of the sodium to be complete. The addition of the ammonium nitrate solution required about fifteen minutes more. The treatment was then complete, excepting for the evaporation of the liquid ammonia, which could easily be ac-

complished by allowing the mixture to stand over night in a hood. The residue could then be dissolved in water the next morning, or at any time convenient, and the determination of the halide made by the Volhard method.

The burettes were standardized by weighing the water delivered by approximately five cubic centimeters on the burette graduations. The volumes were accurately read and from this data a correction curve was plotted. Outside of the ordinary quantitative apparatus, which requires no description, no other equipment was used.

The method finally adopted for all titrations was as follows: to the residue dissolved in 50 cc., of water, add 5 cc., of 10 per cent nitric acid, and run in an excess of standard silver nitrate from the burette. The precipitated silver halide is filtered off and washed until free from silver (usually six washings were sufficient). To the filtrate is added 5 cc., of a clear saturated solution of ferric ammonium sulfate, and the excess of silver nitrate titrated with potassium sulfocyanate until the permanent red tinge is imparted to the solution by one drop of the potassium sulfocyanate. The silver nitrate and potassium sulfocyanate were standardized by the same procedure as given above. Recrystal-

lized, dried, chemically pure salts were used, sodium chloride for chlorine, potassium bromide for bromine, and potassium iodide for iodine, and each of the values for the silver nitrate, which agreed to within .044 per cent, was taken. A mean value for the silver nitrate was then calculated and the solution converted to equivalent grams of chlorine, bromine and iodine, per cubic centimeter. These values were used in all substances investigated. The silver nitrate and potassium sulfocyanate solutions were titrated against each other and the ratio of the two obtained. From this ratio the value of one cubic centimeter of the sulfocyanate in cubic centimeters of the silver nitrate was found, and all volumes of potassium sulfocyanate were converted to equivalent volumes of silver nitrate by multiplying by the factor. No attempt was made to have the solutions tenth normal or fortieth normal, because of the shortness of time for the work. The fortieth normal solutions were made by diluting 250 cc., of the two tenth normal solutions to one liter. These two fortieth normal solutions were then titrated against each other for their ratio and the silver nitrate standardized by titrating it with the tenth normal potassium sulfocyanate. This value was converted from grams of silver nitrate

to its equivalent in grams of chlorine, bromine and iodine per cubic centimeter.

The classes of substances treated were of three general types: (1) the aliphatic hydrocarbon derivatives of chlorine, bromine and iodine; (2) the aromatic monocyclic hydrocarbon derivatives of the halides; (3) the polycyclic substances of which only alpha-brom-naphthalene was available. A few other substances were treated, one a sulfur compound to see if sulfur could be determined in this manner, and one a cyanide. One other substance of a complex structure and containing iodine was treated, but owing to there being no fortieth normal solutions on hand at the time it was studied, no results of any value could be obtained without using excessively large quantities of the substance. As the total amount was not over two grams, no further attempts were made with it, because of the substance being needed for other work. The object of studying this substance was to find out the effect of high percentages of carbon upon the reactions in the method.

Of the aliphatic series, a saturated derivative of chlorine, bromine and iodine were studied. The substances used as representatives of this class were

chloroform, bromoform and iodoform. As a representative of the olefine class, ethylene bromide was used, and as a representative of the chlorine acids, monochlor-acetic acid. An acid chloride was desired, but none with an aliphatic residue could be obtained from the stock in a pure state, and no time was available to prepare one.

Of the aromatic hydrocarbons of the monocyclic derivatives, a chlorine, bromine and an iodine compound was obtained having the halide attached directly to the ring. The substances used were parachloronitrobenzene, iodobenzene and ortho-bromtoluene. In this class of hydrocarbons an acid chloride was obtained, the one used being benzoyl chloride.

Of the polycyclic aromatics only alpha-bromnaphthalene was obtained. Of the miscellaneous substances, the cyanide was tolyl cyanide, the sulfide was para-brom-phenyl-thiourea. The other substance with the high carbon content was para-iodobenzene-phenyl-formamidine.

Results.

The accuracy of the results are in several cases very poor, and in only a few instances are they passably good. But with the knowledge of analytical procedure gained, and from the errors and discrepancies noticed in writing this article, I believe that the method can, with very little difficulty, be refined to such an extent as to make the results accurate to within two tenths of one per cent.

Substance: Iodoform.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error, Per Cent.
1.	96.43	96.19	0.24
2.	96.43	95.66	0.77

Notes. The substance dissolved in liquid ammonia to give a slightly yellow solution. Upon the addition of metallic sodium, the solution becomes the color of iodine vapor, but remains transparent until the sodium is in excess, when the solution becomes opaque, viscous and deep blue in color. Upon the addition of ammonium nitrate solution, the mixture becomes mobile and light yellow in color. After the evaporation of the ammonia, a slight odor of isocyanides is noticeable.

Substance: Chloroform.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	87.07	81.82	5.25
2.	87.07	Lost by spattering, when nitrate was added.	
3.	87.07	Over 100%	
4.	87.07	55.73	31.34
5.	87.07	87.97	0.90
6.	87.07	84.84	2.23
7.	87.07	87.75	0.68
8.	87.07	87.28	0.21
9.	87.07	85.76	1.31
10.	87.07	96.80	9.73

The chloroform dissolved, forming a clear colorless solution. Upon treating with sodium, a vigorous reaction takes place, if the surface of the sodium is clean, to a colorless solution until the sodium is in excess; then a deep blue viscous liquid is formed. Upon acidulation with ammonium nitrate solution, the liquid becomes mobile and pale yellow in color. Upon evaporation, the odor of moldy wood is noticeable. Trials numbered from one to four, inclusive, were made using a pycnometer for holding the chloroform. In trial number three, the ammonium nitrate was not added to the

ammonia solution, but the aqueous solution of the residue was acidulated with the usual amount of nitric acid, which did not make the solution acid, thereby causing the high result. In trial number three, the ammonium nitrate was left out accidentally, but in number ten it was left out intentionally, and the aqueous solution acidulated, with the discrepancy in the result noted. In trials six and nine, an oily residue was left, probably due to not allowing the sodium sufficient time to react in the reduction stage. In trial number two the ammonium nitrate was added in the solid state, which caused spattering. Afterwards all the ammonium nitrate was dissolved in liquid ammonia and added slowly with a pipette.

Substance: Bromoform.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	94.81	97.41	2.60
2.	94.81	Lost by spattering, when nitrate was added.	
3.	94.81	Spilled.	
4.	94.81	88.03	6.78
5.	94.81	101.50	6.69
6.	94.81	Lost because the Dewar tube exploded.	
7.	94.81	95.39	0.58

8.	94.81	93.83	0.98
9.	94.81	Over 100%, because solution was alkaline.	
10.	94.81	Over 100%, because solution was alkaline.	

Bromoform solidifies upon its addition to liquid ammonia, if enclosed in a bulb, but if added directly it dissolves to a colorless solution without any noticeable reaction. Upon the addition of sodium, no color is formed until the sodium is in excess, but a vigorous reaction takes place. When the sodium is in excess, the characteristic blue color and a viscous liquid is formed. The solution again becomes mobile upon the addition of the ammonium nitrate, to form a colorless solution when the reduction was complete. Upon the evaporation of the liquid ammonia, no odor was noticeable.

In the first four trials, the pyknometer method was used, but this was later abandoned for the sealed bulb method. In the first trial; the bromoform had become dark brown on account of the action of light. It was purified by recrystallization, and then melted and placed in a pyknometer painted with a black dye dissolved in amyl alcohol until deep enough to be opaque. This method preserved it from coloring, and was used for keeping it during all of the work. For the later work,

a small quantity was removed from the pyknometer into a small tube as needed. The material not used was discarded. In trials five and six, it was noticed to be slightly colored but was used, and this probably accounts for the high value obtained in five. The Dewar tube was destroyed in number six. This damage was caused by the heat generated in adding the ammonium nitrate solution. The liquid ammonia solution of ammonium nitrate was poured down the side of the tube and began to react with some of the products that had dried on the wall of the tube. The heat generated produced light, and some of the cold solution following struck the hot tube and caused it to crack. This was followed by an explosion which shattered the tube. Trials numbered seven and eight were used with some of the bromoform recrystallized again, and gave fair results. Trials nine and ten were left at the same time as the chloroform number ten, and the ammonia was allowed to evaporate from them while in the reduction stage.

Substance: Ethylene Bromide.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	85.06	80.45	4.61
2.	85.06	83.92	1.14

3. 85.06 84.44 0.62

The ethylene bromide used was prepared by a student in the organic chemistry department. After he had purified it by fractional distillation, it was recrystallized three times and the last crop of crystals dried and used. It was kept in a darkened pyknometer, as was the bromoform, but the first two trials were run by weighing it from the pyknometer. The last trial was made by using a bulb, but the stoppers on the pyknometer came off after this trial and allowed the ethylene bromide to syphon out when the pyknometer was left on its side over night.

The ethylene bromide solidifies on being put into liquid ammonia if enclosed, but dissolves when added directly. It gives a colorless solution in the neutral condition, and also with sodium, until the blue color shows an excess of sodium. Its solution, when acid, is also colorless, and the residue left by evaporation is odorless and white, and should leave no oily residue when the reaction is complete. The reaction with sodium is very vigorous.

Substance: Monochlor-acetic Acid.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	37.53	36.86	0.67
2.	37.53	37.23	0.30
3.	Determination lost; stop-cock leaked on burette.		

The crystals of pure monochlor-acetic acid were weighed by difference from a weighing bottle kept in a desiccator, and were dropped directly into the Dewar tubes. The crystals dissolve with a noticeable evolution of heat to a colorless solution. This solution remains colorless upon the addition of sodium, but when an excess is present a vigorous reaction takes place. The excess of sodium is told by the usual blue color. When acidulated with ammonium nitrate the reaction takes place vigorously, and if any of the dry residue is acted upon by the ammonium nitrate, light is evolved. The residue after evaporation of the liquid ammonia is white, with no odor or oil noticeable

Substance: Ortho- brom-toluene.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	46.73	47.59	+ 0.86

2.	46.73	46.46	- 0.27
3.	46.73	46.47	- 0.26
4.	46.73	46.20	- 0.53

The substance used was Kaulbaum's ortho-brom-toluene. It solidifies upon being placed in the liquid ammonia if enclosed, but dissolves readily when in contact with the solvent. When acted upon by sodium no color is produced until the sodium is in excess, when the usual blue color is formed. The reaction with sodium is moderately vigorous. Upon adding ammonium nitrate, a fairly vigorous reaction takes place to a light yellow colored solution when the reduction is complete. Upon the evaporation of the ammonia, an oily residue is left, which is soluble in benzene and has the odor of benzene. The water soluble portion of the residue has a faint yellow color.

Substance: Para-chlor-nitro-benzene.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	22.53	22.61	0.08
2.	22.53	22.58	0.05

The para-chlor-nitro-benzene had been pre-

pared and carefully purified by some former students of the department, and was used just as obtained, with the exception that the crystals were ground in an agate mortar to facilitate solubility. The substance was weighed directly into the Dewar tubes from the weighing bottles, and the liquid ammonia added. A blue solution was formed, of the same color as liquid oxygen when the latter is obtained by the evaporation of liquid air. The substance was not readily soluble when the ammonia was present, but upon the addition of the sodium it gradually dissolved as the portion in solution was reduced by the sodium. The reaction was not vigorous, but proceeded slowly. On the addition of a small amount of ammonia, then sodium, and then of more ammonia, the solution took place more rapidly, but still the reduction proceeded slowly. Upon adding sodium, the color was at first a light brown, which became a deep reddish brown as more sodium was added, this latter color remaining until the reaction was complete, when the characteristic blue color was formed, showing an excess of sodium present. This blue color was permanent when any of these substances was treated and remained as long as there was any of the solvent present. The solution was viscous and did not change very much upon the addition of ammonia. The time required for the

reduction of para-chlor-nitro-benzene in a quantity feasible for use with tenth normal silver nitrate was about one hour. Upon the addition of ammonium nitrate the solution became mobile and caramel colored, but clear. A slight odor of isocyanide was noticeable when the residue, left after the evaporation of the ammonia, was examined, and a thick light brown colored oil was formed, which was not soluble in water, but readily so in benzene. The water soluble portion of the residue had a slight yellow color.

Substance: Benzoyl chloride.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	25.24	23.44	-1.80
2.	25.24	22.53	-2.71
3.	25.24	24.96	-0.28

The three results given were made using tenth normal solutions. Two more determinations were made, using fortieth normal standard solutions.

Results with fortieth normal solutions:

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
4.	25.24	25.28	0.04
5.	25.24	26.17	0.93

The benzoyl chloride was secured from Dr. Dains' stock of organic chemicals, and, being Kaulbaum's product, was not purified. The material gave some trouble in sealing the capillary of the bulbs, on account of its being readily decomposed by heating. At the tip of the tube, it would always leave a small black deposit caused by the destruction of the small quantity adhering to the inner wall. The outer wall was wiped with a clean cloth to remove any of the substance adhering to it after filling the bulb and before sealing the capillary.

The benzoyl chloride became solid when the bulb was placed in liquid ammonia, and, upon crushing the bulb, a vigorous reaction took place, white fumes being formed. An attempt was made to collect these fumes, but without success. The benzoyl chloride was easily soluble, and, when the sodium was first added, a yellow color was produced, accompanied by a vigorous reaction. By allowing the excess sodium solution to stand for thirty minutes, and then acidulating with ammonium nitrate, a transparent salmon colored solution was formed, leaving no odor or oily residue upon evaporation. The water solution was pale yellow in color. In trial number two, an oily residue was left. In trials

four and five, the fortieth normal solutions were used, to avoid the difficulty attending the making and filling of such large bulbs as were necessary if tenth normal solutions were used. In each trial the fumes were given off, but apparently they did not contain any of the chlorine, as is indicated by the analyses.

Substance: Alpha-brom-naphthalene.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	38.61	30.11	8.50
2.	38.61	38.42	0.19
3.	38.61	39.08	0.47
4.	38.61	34.65	3.96

The alpha-brom-naphthalene was Merck's chemically pure, obtained from Dr. Tillotson, of the Department of Industrial Research. In the first two trials, tenth normal solutions were used, but in the last two the fortieth normal ones were used. The reason for this change was given under the discussion accompanying the data for benzoyl chloride. In addition to the reason stated there, the quantity of material available was small and was needed for other work.

The alpha-brom-naphthalene is a solid at the temperature of liquid ammonia, and readily dissolves

to a colorless solution. The solution remains colorless upon the addition of sodium, until the latter is in excess. After acidulating the solution in liquid ammonia becomes pale yellow in color.

The trial numbered one left a dark brown oily residue after the reduction and acidulation, which was not soluble in water, but was soluble in benzene. This oil had the odor of the original substance. In trial number two there was no oily residue, and the residue left after the evaporation of the liquid ammonia was completely soluble in water, to a light yellow colored solution. In trial three, there was no oily residue. Number four left the oily residue because it was not left standing in the reducing condition for sufficient length of time. This compound requires, in order that the reduction be complete, standing in the excess of sodium solution for at least thirty minutes. At the end of that time the solution must still have the blue color. The two cases where an oily residue was left gave low results, as is shown by the table. In trial number three, some of the material charred during the sealing of the tube. That this charred material was on the inside of the tube was shown by scraping the outside, which yielded nothing. This charring probably

caused some of the decomposed material to escape without removing its proportional bromine content, and gave a high result as a consequence.

Substance: Iodobenzene.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	62.21	61.84	0.37
2.	62.21	60.56	1.65
3.	62.21	60.90	1.31

The iodobenzene used was prepared by diazotizing aniline by the method given in Gattermann's "Practical Methods of Organic Chemistry". The iodobenzene was dried and distilled, the fraction boiling between 187° and 188° C., being used. On putting the iodobenzene into the liquid ammonia it solidifies, but when in contact with the solvent it dissolves to a colorless solution. When the sodium is added, the characteristic color of iodine vapor is formed. When the sodium is in excess, the blue color is produced. The solution, before containing an excess of sodium, is transparent. After acidulation, the solution becomes mobile and transparent, but yellow in color. The residue left after the evaporation of the ammonia contained an oily substance which had the odor of benzene and is not soluble in water

but was soluble in benzene.

On the second trial, some of the water, used in washing the precipitated halide, spilled on the stopper of the filter flask, and entering the flask caused a slight cloudiness, due to the precipitation of silver, which gave the low result. In trial number three, the precipitated silver iodide was not finely divided, and, by holding some of the silver nitrate enclosed, gave the low result. The remainder of the iodobenzene was accidentally lost and, as the time was very limited, no more could be made. The only reason for making the iodobenzene was that no iodine derivative of the aromatic hydrocarbons could be obtained from the chemical department.

Substance: Tollyl cyanide.

Trial No.	Theoretical Per Cent.	Determined Per Cent.	Error Per Cent.
1.	22.26	Lost.	
2.	22.26	13.18	9.08

The tolyl cyanide was weighed in bulbs and dropped into the liquid ammonia, solidifying upon striking the solvent. The cyanide dissolved without any noticeable reaction to a clear solution. Upon the addition of the sodium, no color change could be noticed un-

til the metal was in excess, when the characteristic blue color appeared. The reaction proceeded with moderate vigor. These two trials were left to react in the reducing condition over night, on account of the laboratory door being accidentally locked. As the ammonia had evaporated by the time they could be reached the next morning, the residue was dissolved in water and titrated. In titrating the first trial, the nitric acid was added before the silver nitrate, and no precipitate was formed upon adding the silver solution. The second trial was treated by taking the aqueous solution of the residue and adding the silver solution to it, without first neutralizing the alkalinity, producing the discrepancy noted. This error was caused by the solubility of the silver cyanide in the alkaline solution of the residue. There was no oily residue found in either trial. No further attempts were made, because the time was exhausted for carrying out this work.

Substance: Para-iodo-benzene-phenyl- formamidine.

Trial: Only one trial was made of this material, because the supply was very small, and its properties are unknown because of its being a new substance. Furthermore, as Dr. Dains, who kindly allowed me to try

this substance, wished to identify more of its properties. no other attempts were made, because with tenth normal solutions such large amounts were required that no more could be spared. The substance easily dissolves in the liquid ammonia to a colorless solution, which becomes violet upon the addition of sodium. An excess, however, produces the usual blue color. When treated with ammonium nitrate, the solution becomes clear and yellow colored. The evaporation of the solvent leaves a slightly oily residue which has the odor of benzene. The water solution of the residue is pale yellow in color. The result obtained was, theoretical per cent, 39.29, determined per cent, 37.57, per cent of error, 1.72.

Substance: Para-brom-diphenyl-thiourea.

In this case an effort was made to see if it would be possible to determine sulfur by this method. The time for my work was exhausted when one trial was completed, so no further work could be done. The reduction in the only attempt made was not entirely to the sulfide, a part going to free sulfur. This free sulfur could not be oxidized to the sulfate for precipitation by barium chloride.

The other observations made showed the

material to be fairly soluble to a colorless solution, which became pale yellow when sodium was added. The usual blue color was later produced, but the reduction apparently went on very slowly at this stage, and was evidently not complete when the reaction mixture was acidulated. The solution was left standing in the blue color for thirty minutes before adding the ammonium nitrate solution. The color of the acidulated solution was pale yellow, and the residue after evaporation of the ammonia was covered with an oily substance, very dark brown in color, and with an odor similar to that of the wash liquor from gas plants. This oil was not water soluble, but easily dissolved by benzene.

Conclusion.

In conclusion, a short summary of the applicability of this method to all classes of organic compounds containing the halides will be given.

In the aliphatic compounds the reaction is very rapid and quite reliable if care is used. The method is much simpler and more rapid than any other in use, and requires very little equipment not in daily use.

In the aromatic compounds, the reaction progresses somewhat slower, but it is quite accurate. The only main difference is the formation of an oily residue in many cases, but this can probably be eliminated by letting the reaction continue longer in the reduction stage. This oily residue was absent in several cases for the aromatic and cyclic compounds, as a review of the data will show.

The only class of cyclic compounds which showed any marked tendency toward offering a serious difficulty to the method were the compounds containing a large percentage of nitrogen. The solubility of these same substances is also of a lower value than that of any of the other substances examined. Whether this same effect would be shown by members of the aliphatic series

containing nitrogen as well as halides was not investigated. This general retarding effect of nitrogen was not noticed at the time the work was being carried out, or it would have been investigated.

In two of the substances studied a large percentage of carbon was present, but in the only one investigated very extensively, namely, alpha-brom-naphthalene, this seemed to have no effect.

This method also indicates that it may possibly be extended to include both the organic cyanides and sulfides. The principle points which still remain to be accomplished are the complete elimination of the oily residue, thus insuring a complete reduction of the compound, and a study of more of the halogen compounds containing nitrogen, to see if there is a limited scope placed upon the method by this element. Of course, the refinement of the method, in order to secure accuracy of the results is to be desired first, but this is evidently more the factor of the operator than of the method.

Then, too, but without the range of this article, comes a study of the products formed at the various stages of the method, and the reactions which take place in the production of these changes and products.

In closing, I wish to express my appreciation of the assistance given me by Dr. Dains and Dr. Tillotson, in placing at my convenience all of the chemicals in their charge, which might be useful in my work. But especially I wish to thank Dr. Gady for having suggested this study, and for the very great assistance he has given me in my efforts.