THE MICRO DETERMINATION OF HALOGENS BY THE CARIUS METHOD

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BY THE
CARIUS METHOD

By

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INTRODUCTION

There are numerous methods available for the micro determination of halogens in organic compounds.

Among these is the Pregl (1) combustion method. This involves the burning of the compound in a stream of oxygen. The products of combustion pass over red hot platinum contacts and the halogen is absorbed in sodium carbonate containing sodium bisulphite which reduces any halate present. The halide ion is then precipitated in a nitric acid solution by silver nitrate. The silver halide is then filtered, dried, and weighed. The disadvantage of this method is that it is not suitable for volatile substances and those which decompose with great difficulty.

The sodium peroxide bomb method, as modified by Elek and Hill (2), gives good results. The sample is fused in a micro bomb with a mixture of potassium nitrate, sodium peroxide and sucrose. The fusion is dissolved and any halate formed is reduced by hydrazine sulfate. The halide is then precipitated and weighed as the silver halide. The disadvantage of this method is the difficulty in the handling of liquids and volatile substances.

In the Zacherl and Krainick (3) method, the organic substance is oxidized by a mixture of concentrated sulphuric acid, silver dichromate and potassium dichromate. The halogen evolved is collected in a mixture of 0.01N sodium hydroxide with acid-free hydrogen peroxide and the excess alkali back titrated with 0.01N hydrochloric acid. This is a rapid determination but has the disadvantage that it cannot be used on volatile substances. Iodine cannot be determined by this method.

The Willard and Thompson (4) method involves the oxidation of the sample by fuming sulphuric acid to which is added ammonium persulfate. The halogen is distilled into alkaline arsenite solution and then precipitated as the silver halide. This method is not suitable for the determination of halogens in volatile compounds.

The Steparow method for halogens in organic compounds has been modified by Rauscher (5) so that it can be used for micro analysis. In this method, monoethanolamine or dioxane is used to dissolve the sample. Metallic sodium is added and the mixture refluxed. The solution is then acidified with nitric acid, filtered and the halide precipitated by silver nitrate. The silver halide is then determined gravimetrically.

The first micro Carius determinations were carried out by Emich and Donau (6). Pregl (7) further developed the method. In this method, the organic compound is decomposed by heating with concentrated nitric acid and silver nitrate at a high temperature and under pressure. The silver halide formed is filtered through a filter tube and then dried and weighed. The advantage of this method is that it is adaptable to solids, liquids, and volatile organic halogen compounds. Samples which decompose with difficulty can also be determined by this method.

The main disadvantage of the method as now used is the length of time required for the combustion which is considerably longer than that required for the other methods. Also when volatile compounds are analyzed, the solution contains glass splinters from the capillary containing the sample which makes it necessary for the precipitate to be weighed in a filter tube which is then reweighed after dissolving the silver halide with potassium cyanide solution.

In the Carius method, as in most of the others previously mentioned, the silver halide is determined gravimetrically. However, a weighed amount of silver nitrate may be used and the excess silver ion determined volumetrically. The Volhard method is probably the most used of these volumetric modifications, at least on a macro scale.

The original Volhard (8) method consists of acidifying a solution of the halide with nitric acid. To this is added a measured excess of standard silver nitrate to precipitate the halide and a quantity of a ferric ion solution which acts as the indicator. Then without filtering off the silver halide, the excess silver nitrate is determined by titrating with a standard thiocyanate solution.

$$Ag^{+} + CNS^{-} \longrightarrow AgCNS$$
$$Fe^{+++} + 6CNS^{-} \longrightarrow Fe(CNS)_6^{---}$$

This method was found to be inaccurate when determining chlorides. The slower the titration was carried out, the lower were the results obtained.

Burgleman (9) reported that the indistinct endpoint was due to free nitric acid which destroyed the color by oxidizing the thiocyanate ion.

Dreschel (10) found that the ferric thiocyanate complex was decomposed by the silver chloride according to the equation:

$$Fe(CNS)_6^{---} + 6AgCl \longrightarrow 6AgCNS + Fe^{+++}$$

He recommended filtering the silver chloride before titrating the excess silver ion.

Rosanoff and Hill (11) proved that the silver chloride interfered in the determination causing low results and they also recommended filtering off the silver chloride.

Kolthoff (12), however, reports that an error is introduced during the filtration due to the carrying down of silver nitrate by the silver chloride. This error is not dependent upon the concentration of silver nitrate present so one can always deduct 0.7% chloride from the amount found.

Rothmund and Burgstaller (13) suggested the covering of the silver chloride with tolvene or benzene. This method worked fairly well when the chloride concentration was small but Kolthoff claims there is an error of 0.6%

Vander Burg and Koppejan (14) investigated the influence of a few colloids on the Volhard titration. They found that in the presence of soluble starch, gelatin, agar-agar, gum arabic, and gum tragacanth, the red coloration of the ferric thiocyanate complex appears indistinct and too late.

The latest modification of the Volhard method was reported by Caldwell and Moyer (15) who used nitro benzene which forms an insoluble layer over the precipitate and thus prevents the silver chloride from interfering. The authors obtained good results by this method when working on the macro scale.

There are several other methods which have been adapted to the determination of small amounts of silver.

Among these is the titration of silver nitrate with a standard potassium iodide solution using palladious nitrate for indicator as devised by Schneider (16). The silver nitrate is precipitated by the potassium iodide and the slightest excess of potassium iodide is converted by palladious nitrate to the brown palladious iodide.

A method devised by McLean and Van Slyke (17) involves the titration of the excess silver ion with potassium iodide using starch and sodium nitrite as the indicator. The first excess iodide ion is oxidized to free iodine by the sodium nitrite giving a blue color with the starch.

The object of this work was to study the Volhard method on a micro scale and its application to the determination of halogens in organic compounds in an effort to speed up the Carius method.

REAGENTS

A 0.1N solution of silver nitrate was prepared from solid, chemically pure silver nitrate which had been heated in a platinum dish between the temperatures of 250°-300° for approximately fifteen minutes. This solution was then diluted to the strength desired for the following analysis.

An approximately 0.1N ammonium thiocyanate solution was prepared from C. P. ammonium thiocyanate and was then standardized against the standard silver nitrate solution. More dilute solutions are prepared as desired by diluting the standard ammonium thiocyanate solution.

A 0.01N sodium chloride solution was prepared from C. P. sodium chloride which had been finely ground in an agate mortar and then carefully heated in a platinum dish until all moisture was removed.

A saturated solution of ferric alum indicator was prepared to which was added concentrated nitric acid to clarify the solution.

APPARATUS

Micro burettes

The micro burettes are of 5 ml capacity. They were calibrated by determining the amount of water delivered.. They are graduated in .02 ml and can be estimated to the nearest .002 ml. All burette readings were taken with a magnifying glass.

Micro balance

The Kuhlmann micro balance was used in weighing out all micro samples.

Carius combustion furnace.

The furnace used for the decomposition of all the organic compounds was an electrically-controlled furnace manufactured by the American Instrument Company. With this furnace it is possible to decompose four samples simultaneously.

Weighing tubes

A long stem weighing tube is used for the solid samples. It consists of a soft glass tube of 30 mm. length and 2 mm. diameter to which is fused a glass rod about 11 cm. long. A ground glass fitting top is used in all cases.

For weighing out the liquids a glass bulb is made by drawing out soft glass tubing into a capillary 2-3 mm. in diameter, and then making this into a thin walled bulb.

One end of the bulb is sealed and the other end drawn out to a fine capillary. To the sealed end is fused a glass rod 30 mm. long which facilitates the breaking of the bulb in the combustion tube.

Combustion Tubes

The combustion tubes are made of Pyrex glass about 20 cm. long and 10 mm. in diameter.

EXPERIMENTAL

The purpose of the first part of this work was to study the Volhard method on a micro scale.

Various amounts of standard 0.05N sodium chloride were transferred by a calibrated pipette to a 10 ml. beaker. To each sample was added a few drops of dilute nitric acid and a measured excess of standard 0.05N silver nitrate. The sample was coagulated by careful heating and then filtered by means of suction through a Pregl filter stick into a 50 ml. Erlenmeyer flask. The precipitated silver chloride was then washed with small portions of a 1% solution of nitric acid. Approximately one ml. of the ferric alum indicator was added to the filtrate. The excess silver nitrate was then titrated with the 0.05N ammonium thiocyanate to the first color change. The following results were obtained:

TABLE I

mg. NaCl	ml. $AgNO_3$ 0.05000	ml. NH_4CNS .06268N	mg. NaCl FOUND	Error mg.
5.845	2.610	.460	5.864	+0.019
5.845	2.563	.450	5.842	-0.003
5.845	2.515	.410	5.851	+0.006
5.845	2.690	.550	5.846	+0.001
5.845	2.690	.552	5.840	-0.005
5.845	2.505	.405	5.837	-0.008
5.845	2.551	.440	5.843	-0.002
5.845	2.510	.410	5.833	-0.011

The volume at the time of the titration was between 15-20 mls.

The results obtained in Table I were better than expected because the burettes used can only be estimated to the nearest .002 milliliters and an error of .002 ml. causes an error of .006 mgms. in the calculated results.

Because of the difficulty of getting the endpoint within .002 ml, solutions 0.01N were tried. When a small amount of wash solution was used, the results were consistently low which was probably due to incomplete washing of the precipitate. When more wash solution was used it became necessary to evaporate the filtrate. Inconsistent results were obtained by this method.

Because of the filtering step required in the above procedure, attempts were made to determine the excess silver nitrate in the presence of the silver chloride.

In the following work, determinations were run in an attempt to adapt the Caldwell and Moyer method to the micro scale.

A sample of the standard sodium chloride solution was transferred to a 50 ml. glass stoppered Erlenmeyer flask. The sample was acidified and a measured excess of 0.05N silver nitrate added. Approximately 20 drops of nitro benzene and one ml. of ferric alum indicator was added. This mixture was then shaken for about 60 seconds or until the silver chloride was coagulated and covered by the nitrobenzene. The excess silver nitrate was titrated with the

.05N ammonium thiocyanate.

TABLE II

mg.NaCl.	ml.$AgNO_3$ .05000	ml.NH_4CNS .04850N	mg.NaCl FOUND	Error mg.
2.923	3.500	2.572	2.924	+0.001
2.923	3.500	2.574	2.917	-0.006
2.338	3.400	2.675	2.338	0.000
2.338	3.290	2.565	2.330	-0.008
2.338	3.400	2.678	2.329	-0.009
1.754	2.940	2.374	1.746	-0.008
1.754	3.200	2.680	1.753	-0.001
1.754	2.900	2.370	1.756	+0.002

The results obtained in Table II indicate that the silver chloride has no effect on the endpoint. Upon thorough shaking the silver chloride is removed from suspension and at the time of the titration, the liquid above the precipitate is perfectly clear. The nitrobenzene also seems to have the property of inhibiting the darkening of the precipitate. The volume at the time of the titration was between 15-20 ml.

The main difficulty when using 0.05N solutions is over-running the endpoint. Because of the difficulty of getting the endpoint within .002 ml., more dilute solutions were tried under the same conditions as before, using nitrobenzene to prevent the silver chloride from reacting.

TABLE III

mg. NaCl	ml. $AgNO_3$ .02500	ml. NH_4CNS .02515N	mg. NaCl FOUND	Error mg.
2.338	4.000	2.386	2.338	0,000
2.338	4.000	2.388	2.333	-0.005
1.754	3.100	1.886	1.757	+0.003
2.923	4.000	1.991	2.920	-0.003
2.923	3.716	1.706	2.922	-0.001
1.169	2.810	2.001	1.165	-0.004
1.169	2.020	1.211	1.175	+0.002

A blank of .004 ml. was deducted from the amount of ammonium thiocyanate used. The volume at the time of titration was between 15-20 ml.

Determinations were run on the standard sodium chloride solution using approximately 0.01N solutions of silver nitrate and ammonium thiocyanate. Blank determinations were run using the same volume of solutions and as near as possible the same conditions as when running the chloride determinations. Varying amounts of nitric acid were added to determine whether or not it had any influence on the endpoint.

TABLE IV

Conc. HNO_3 ml.	ml. NH_4CNS .01261N	Volume at Solution ml.
0.1	.012	20
0.2	.011	20
0.5	.012	20
1.0	.011	20
2.0	.012	20
3.0	.014	20
4.0	0.1	20
5.0	0.25	20

Satisfactory blanks cannot be determined when more than 3 mls. of concentrated nitric acid is added. The color of the ferric thiocyanate comples disappears in 5-10 seconds which is probably due to oxidation of the thiocyanate ion by the nitric acid. However, the amount of nitric acid used in all cases is considerably less than 3 ml., so it does not cause inaccurate results.

TABLE V

Mg. NaCl	ml. $AgNO_3$ 0.01000N	ml. NH_4CNS .01216N	Mg. NaCl. FOUND	Error mg.
1.754	4.000	0.797	1.749	-0.005
1.754	3.980	0.777	1.753	-0.001
1.754	4.295	1.018	1.757	+0.003
1.754	4.540	1.217	1.757	+0.003
1.754	4.500	1.197	1.748	-0.006
1.169	4.000	1.582	1.171	+0.002
1.169	4.000	1.587	1.168	-0.001

For all of the above determinations a blank correction of 0.012 ml. was deducted from the amount of ammonium thiocyanate used. The volume at the time of titration was between 15-20 ml.

A number of determinations were run on the standard sodium chloride solution, using varying amounts of nitrobenzene to see if it had any effect on the titrations.

TABLE VI

mg. NaCl	ml. $AgNO_3$ .01000N	ml. NH_4CNS .01216N	Nitrobenzene drops	mg. NaCl FOUND	Error mg.
1.754	4.500	1.199	10	1.750	-0.003
1.754	4.503	1.202	10	1.749	-0.004
1.754	4.540	1.223	20	1.754	0.000
1.754	4.540	1.227	20	1.750	-0.004
1.169	4.000	1.580	30	1.173	+0.004
1.169	4.000	1.580	30	1.168	-0.001

It is evident, as shown by these results, that varying amounts of nitrobenzene has no influence on the results. However, it was found that when the volume of the solution was greater than 35 ml., it was impossible to completely coagulate the silver chloride. When the solution was titrated the silver chloride would interfere, making it impossible to get the proper endpoint.

The Volhard method was found to be adaptable to the micro scale, when using solutions 0.025N and 0.01N. The next step was to determine whether or not it could be used in connection with the micro Carius method.

THE CARIUS DETERMINATION

A 4-8 mgm. sample of the solid organic compound was weighed out in the weighing tube and transferred to the combustion tube containing 10-20 mgms. of accurately weighed silver nitrate. Approximately 0.25 ml. of concentrated nitric acid was added and the tube immediately sealed by means of an oxygen flame. The liquid compounds were drawn into the previously weighed micro bulb by carefully warming the bulb and dipping the capillary into the liquid. On cooling, the liquid will be drawn into the bulb. The capillary was sealed and the tube reweighed. It was then placed in the combustion tube containing silver nitrate and concentrated nitric acid. The tube was sealed as before. The weighing bulb was broken by hitting the combustion tube against the hand. The combustion tubes and contents were placed in the combustion furnace and heated at such a rate that by the end of three hours the temperature had risen to 250°. This temperature was maintained for another three-hour period. The samples were then allowed to cool. The combustion tube was pulled part way out of the furnace and the tip heated with a small flame to drive out the condensed liquid. It was then heated strongly and the pressure inside the tube caused it to break at the weakened point.

The contents of the tube were flushed out with small portions of hot water into a 50 ml. glass-stoppered Erlenmeyer flask. Approximately 10 drops of nitrobenzene and one ml. of ferric alum indicator were added to the flask and the mixture thoroughly shaken for 60 seconds. The excess silver nitrate was then titrated with 0.025N ammonium thiocyanate.

For halogen compounds containing bromine and iodine, no nitrobenzene was added because the solubility of silver bromide and silver iodide is less than that of silver thiocyanate.

Analyses were run on a number of organic halogen compounds with the following results:

TABLE VII

SAMPLE	Sample mg.	AgNO$_3$ mg.	ml. NH$_4$CNS .02515	Theor %	Calculated % halide
Chloro-benzoic Acid	5.349	11.675	1.372	22.64	22.63
	5.067	17.135	2.714		22.69
	4.816	10.713	1.281		22.65
	7.060	17.445	2.280		20.60
Chloro acetanilide	4.725	12.416	1.796	20.91	20.86
	4.002	9.812	1.355		20.91
	8.411	13.294	1.144		20.85
	6.028	10.337	0.995		21.01
	5.457	9.941	1.056		20.84
	5.755	14.269	1.991		20.82
	8.875	15.436	1.535		20.84
p.p. dichloro-azoxy benzene	7.000	23.177	3.305	26.55	26.89
	4.318	13.246	1.796		26.84
	5.513	17.058	2.339		26.65

TABLE VIII

SAMPLE	Sample mg	AgNO$_3$ mg	ml. NH$_4$CNS .02515	Theor %	Calculated % halide
βchloro Anthraquinone	5.140	12.337	2.031	14.61	14.71
	6.936	16.067	2.612		14.67
	5.111	8.235	1.084		14.66
p-Bromo Acetanilide	4.674	12.286	1.994	37.33	37.60
	4.704	12.096	1.955		37.41
	6.145	16.094	2.610		37.63
p-bromo Diphenyl	4.355	8.676	1.250	34.28	35.85
	7.931	10.977	1.211		34.34
2 Cl-5-Hydroxy-toluene	4.195	11.001	1.400	24.86	24.95
	8.852	21.645	2.565		25.13
	5.602	11.566	1.115		25.15
m-chloro phenol	4.577	11.166	1.180	27.58	27.86
	4.110	10.794	1.250		27.62
Iodobenzoic Acid	6.320	11.171	1.593	51.17	51.39
	8.635	9.848	0.913		51.34
	7.388	11.225	1.437		51.27

The following determinations were run using the same procedure as before with the exception that 0.01N ammonium thiocyanate was used to titrate the excess silver nitrate.

TABLE IX

SAMPLE	Sample mg.	AgNO$_3$ mg.	ml. NH$_4$CNS .01261N	Theor %	Calculated % chloride
Chloro acetanilide	6.684	10.490	1.770	20.91	20.91
	6.648	9.613	1.380		20.89
	4.266	11.195	3.220		21.01

The main disadvantage of the Carius method, as used in the previous analyses, is the time required for the decomposition of the sample. The six hours required is considerably greater than the time necessary for the other methods of determining organic halogens, thus decreasing the value of the Carius method for routine analysis.

Because of this, attempts were made to speed up the determination by increasing the temperature and decreasing the time of combustion. On the following trials the temperature was raised to 300° in 60 minutes and then h held at that temperature for another 60 minutes. The conditions for the titration are the same as before using .01N ammonium thiocyanate.

TABLE X

SAMPLE	Sample mg	AgNO$_3$ mg.	ml. NH$_4$CNS .01261N	Theor %	Calculated % halide
Chloro acetanilide	4.300	10.675	2.955	20.91	21.00
	6.417	13.394	3.245		20.94
Chloro benzoic Acid	5.166	9.168	1.655	22.64	22.71
pp dichloro-azoxy benzene	5.391	9.975	1.430	26.55	26.75
	5.880	11.602	1.915		26.60
p bromodiphenyl	3.535	9.399	3.180	34.28	34.35
	4.856	13.343	4.570		34.26
bromoacetanilide	4.080	10.594	3.430	37.33	37.88
	3.622	13.458	4.920		37.84
2 chloro 5-hydroxy-toluene	5.009	14.092	3.775	24.86	24.95
	6.279	11.749	1.975		24.98

These results show that the time required for the decomposition can be decreased. In all the above analyses the samples were completely decomposed by a two-hour combustion period thus considerably decreasing the time required for the Carius determination.

SUMMARY

A modified micro Carius method for determining halogens in organic compounds using the Volhard method to determine the excess silver nitrate was found to give good results.

The Volhard method, using 0.025 and 0.01N solutions, was modified by using a small amount of nitrobenzene which makes it possible to carry out the titration in the presence of the silver chloride. It is not necessary to use nitrobenzene when analysing compounds containing bromine and iodine.

It was found that the organic halogen compounds were completely decomposed by a two-hour combustion period as compared to the six hours previously required, thus considerably decreasing the time required for the Carius determination.

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