THE DETERMINATION OF PERCHLOROMETHYL MERCAPTAN IN LOW CONCENTRATIONS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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THE DETERMINATION OF PERCHLOROMETHYL MERCAPTAN IN LOW CONCENTRATIONS

I. INTRODUCTION

The purpose of the investigation was to find a method for the decomposition and analysis of perchloromethyl mercaptan in low concentrations. To this end fusion or combustion methods could not be applied. On the choice of a method it was necessary to have an absorbing solution to decompose perchloromethyl mercaptan in the cold. It was desirable to have a method in which the absorbing solution could be introduced into a bottle containing a sample of perchloromethyl mercaptan thereby decomposing the compound and making possible the analysis of the chloride ion formed. Due to the low amount of gas present in a sample, an absorbing solution that contained a high chlorine content (high blank) could not be used. The analysis of a low concentration depends upon the percentage of chlorine present. To find a suitable method for the determination of perchloromethyl mercaptan it was necessary to study the properties and reactions of this compound. In this manner a suitable method was developed by using alcoholic sodium sulfite. Contrary to the statement in the literature[7] that potassium hydroxide decomposes perchloromethyl mercaptan it was found not to be quantitative for low concentrations.

7. Rathke, B. (Berichte 3, pp. 860 (1870)).

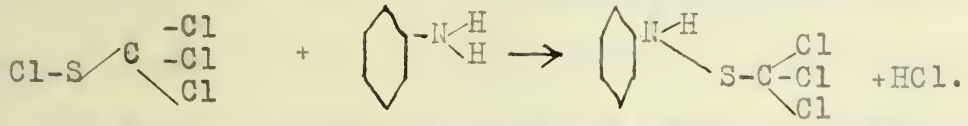
II. PROPERTIES

Perchloromethyl mercaptan is a yellow oil with an unpleasant, pungent odor. As usually obtained, however, it has a dark red color. Its odor is indistinguishable from that of sulfocarbonyl chloride ($CSCl_2$). Sometimes it occasions a copious flow of tears. It attacks the membranes of the throat and causes irritation and coughing. Perchloromethyl mercaptan boils at 146°-148° C (corrected) and has a specific gravity of 1.6953 at 17.5°C or 1.7120 at 0°C. It boils with little decomposition at 149°.[8]

Perchloromethyl mercaptan is acted upon by silver at 160°C to give sulphocarbonyl chloride. If perchloromethyl mercaptan is treated with water at 160°C in a sealed tube it decomposes very readily giving carbon dioxide, hydrochloric acid, and free sulfur. With ammonia the reaction is quite similar; but the greater portion of the sulfur is precipitated and at the same time ammonium sulphocyanate is formed, together with a solid substance containing sulfur and nitrogen, which, after the removal of the sulfur by carbon disulphide, appears as a light yellowish brown powder which is insoluble in any menstruum. Potassium iodide acts rapidly on perchloromethyl mercaptan even in the cold, with the formation of hydriodic acid and the liberation of iodine leaving a small quantity of a tough yellowish white solid substance. Nitric acid (specific gravity 1.2) when poured on perchloromethyl mercaptan changes it in the course of two or three weeks into a white solid substance melting at 135°C, and having the other properties of

8. Rathke, B. (Ann. Chem. 167, p. 195 (1873)).

trichloromethyl sulphochloride, CCl_3SO_2Cl (in the ordinary process for the preparation of this latter substance it is evidently produced by the oxidation of the perchloromethyl mercaptan ($CSCl_4$) first formed). With aniline, perchloromethyl mercaptan combines to form trichloromethyl mercaptoaniline:



Perchloromethyl mercaptan when treated with a concentrated solution of potassium sulphite decomposes into potassium chloride and a salt, $C(SO_3K)_3$-SH.

Perchloromethyl mercaptan is insoluble in water, alcohol and most all of the ordinary solvents. It dissolves in petroleum ether, which is perhaps its best solvent. It also dissolves slowly in ether, when a relatively large proportion of the menstruum is used.

III. DISCUSSION

According to Albrecht, when perchloromethyl mercaptan is treated with a concentrated solution of potassium sulphite, it evolves considerable heat, and after a time solidifies to a crystalline pulp, which on recrystallization yields large crystals of a rather difficultly soluble salt $C(SO_3K)_3$-SH. This salt might be called potassium methylmercaptan trisulphate. The reaction of potassium sulphite on perchloromethyl mercaptan is probably as follows:

$$5K_2SO_3 + CCl_3SCl + HOH \longrightarrow 4KCl + C(SO_3K)_3SH + K_2SO_4 + KHSO_3$$

With this reaction as a basis a quantitative method was developed for the determination of perchloromethyl mercaptan.

Both direct and vacuum bottle methods of decomposition were used. The vacuum bottle method similated conditions for collecting samples in the field as closely as possible. The direct method was tried out first with satisfactory results and the perchloromethyl mercaptan was then determined by the vacuum bottle method. The direct method consisted in placing a sealed glass bulb containing a weighed amount of the liquid "gas" into a half liter, glass stopped bottle, the absorbing solution was introduced and also a few glass beads to facilitate breaking of the bulb by shaking. The bottle was stopped, shaken, and allowed to stand for at least two hours and was then opened and the contents analyzed for the chlorine present according to the procedure outlined. The vacuum bottle method was carried out in a somewhat similar manner. Two and one-half liter acid bottles were used. After the weighed bulb containing the sample was introduced, the bottle was evacuated and the bulb was broken by shaking the bottle. In this manner all the perchloromethyl mercaptan, volatilized because of its high vapor pressure; thus a "gas" sample was obtained which simulated field sampling. By means of the vacuum the absorbing solution was drawn in the bottle, shaken, and after standing over night was analyzed for the chlorine present.

IV. EXPERIMENTAL

A sample of perchloromethyl mercaptan in the gaseous form was obtained by drawing the same from a gas chamber into an evacuated bottle, or, by placing a weighed bulb of perchloromethyl mercaptan into a two and one half liter bottle, which was then evacuated. On breaking this bulb the perchloromethyl mercaptan was vaporized, giving a definite gas concentration in the bottle.

Fifty cubic centimeters of 7% alcoholic sodium sulphite solution were drawn into the bottle, and the same was thoroughly shaken and allowed to stand over night. Most of the vacuum was released before shaking was completed.

After absorption the solution was carefully washed into a 500 cc Erlenmeyer flask and the alcohol was evaporated off on a steam bath. Ten to 15 cc of concentrated nitric acid (sp. gr. 1.43) were added and the solution was boiled to drive off the sulfur dioxide. An excess of standard silver nitrate solution was added and the solution was boiled to coagulate the precipitate, filtered and cooled. The excess silver nitrate was determined by titration with standard sodium thiocyanate, using ferric alum as an indicator. A blank determination was always made and allowed for.

The sodium sulphite solution was made as follows: 21 grams of sodium sulphite were dissolved in 200 cc of water, and when ready for use, 100 cc of 95% alcohol was added. This gave a 7% solution. The alcohol may be added at once to the sulphite, thus giving a stock solution, but due to the fact that the sulphite has

a tendency to crystallize, it was found very convenient to add the alcohol just before using.

The purity of the samples of perchloromethyl mercaptan used was determined by the fusion method in a Parr Peroxide Bomb[1] with sodium peroxide and potassium nitrate, determining the chloride thus formed by the Volhard method. The percentage of purity was taken into consideration in figuring all results.

The following results were obtained by the vacuum bottle method:

Table I.

SUMMARY OF RESULTS ON
VACCUUM BOTTLE DETERMINATION OF GASEOUS PERCHLORO-
METHYL MERCAPTAN

Weight perchloromethyl mercaptan	Cap. Bottle	Gm. Cl. Theor.	Gm. Cl. Found	% Cl. Found	% Decomp.	Perchloromethyl mercaptan per liter	Concentration
0.0231	2500cc	0.0176	0.0175	75.75	100.60	0.00924	1/1080
0.0339	"	0.0259	0.0253	74.54	98.76	0.01356	1/739
0.0391	"	0.0298	0.0292	74.94	99.07	0.01564	1/640
0.0351	"	0.0268	0.0260	74.13	98.20	0.01404	1/712

The method of analysis was given to three different observers who determined perchloromethyl mercaptan according to the above proceedure and accurate and consistent results were obtained by these observers, thus showing that the method was easily applicable for the determination of low concentrations of perchloromethyl mercaptan.

1. Parr, S. W. (J. Ind. & Eng. Chem. 11, 230 (1919)).

The results obtained by the three men were as follows:

Table II.

SUMMARY OF RESULTS ON
VACUUM BOTTLE DETERMINATION OF GASEOUS PERCHLORO-
METHYL MERCAPTAN BY THREE DIFFERENT OBSERVERS.

Weight perchloromethyl mercaptan	Cap. Bottle	Gm.Cl. Theor.	Gm.Cl. Found	% Cl. found	% Decomp.	Perchloromethyl mercaptan per liter	Concentration
			Observer 1.				
0.0195	2500cc	0.08234	0.08143	74.64	98.80	0.0437	1/229
0.0416	"	0.03139	0.03114	74.70	98.90	0.0167	1/600
0.0456	"	0.03441	0.03414	74.31	99.10	0.0182	1/550
0.0979	"	0.07389	0.07308	74.62	98.80	0.0392	1/255
0.0519	"	0.0391	0.03876	74.67	98.90	0.0208	1/482
0.0378	8500cc	0.02853	0.02831	74.90	99.20	0.00445	1/2250
			Observer 2.				
0.0415	2500cc	0.00317	0.00311	75.03	99.39	0.0166	1/600
0.0476	"	0.00363	0.00360	75.58	100.12	0.01910	1/525
0.0234	5300	0.00178	0.00179	75.46	99.96	0.00441	1/1800
0.0148	3400	0.00129	0.00112	75.67	100.23	0.00435	1/1900
			Observer 3.				
0.0328	2500	0.0250	0.0249	75.81	98.88	0.01312	1/630
0.0131	"	0.0100	0.0099	75.76	99.30	0.00524	1/1900
0.0150	"	0.0114	0.0113	75.33	98.74	0.00600	1/1400
0.0173	"	0.0132	0.0131	75.72	99.25	0.00692	1/1200
0.0197	"	0.0150	0.0148	75.12	98.46	0.00788	1/1050
0.0301	"	0.0230	0.0229	76.08	99.72	0.01204	1/700

The action of alcoholic and aqueous solutions of sodium peroxide, sodium hydroxide, and potassium hydroxide were then carefully studied. In this study the amount of alcohol, the amount of reagent and the procedure were varied so as to give the best possible results. Both direct and vacuum bottle methods were used. The strength of the aqueous sodium peroxide was varied from 5 to 20%,

(a 26% solution of Na_2O_2 at 20°C is a saturated solution). The alcoholic sodium peroxide was likewise varied from 5 to 20% in a 15% alcoholic solution. The aqueous potassium hydroxide solution was varied from 3 to 5%, and the alcoholic sodium hydroxide was varied from 3 to 10% in a 50% alcoholic solution. The results show that these reagents cannot be used for the determination of perchloromethyl mercaptan, for in no case were the results quantitative.

A. In the following the direct absorption method was used:

(1) The action of aqueous sodium peroxide on perchloromethyl mercaptan.

(a) 5% sodium hydroxide solution in water.

Fifty cubic centimeters of a five per cent aqueous solution of sodium peroxide (made by dissolving 10 grams of Na_2O_2 in 200 cc of H_2O) were introduced into a 500 cc glass stoppered bottle containing a weighed bulb of perchloromethyl mercaptan, the bottle sealed with paraffin, and shaken until the bulb of perchloromethyl mercaptan was completely broken. One bottle was shaken every twenty minutes for 4 hours and then opened and the halogen determined as given in the 7% Na_2SO_3 method. Two other bottles were allowed to stand over night. The following results were obtained.

Table III

Time	Sample of Perchloromethyl mercaptan	% Cl. Found	% Cl. Theoretical	% Decomposition
4 hours	.0226 gms.	29.35	76.295	38.46
Overnight	.0308 "	31.49	76.295	41.26
Overnight	.0302 "	37.74	76.295	49.44

(b) 20% sodium peroxide solution in water.

Fifty cubic centimeters of 20% Na_2O_2 in water (40 grams Na_2O_2 in 200 cc. of water) were also used as a decomposing agent. The same procedure was carried out as in I (a) with the exception that all the bottles stood overnight. Results:

Table IV

Wt. of Perchloromethyl mercaptan.	Grams Cl. Found	% Cl. Found	% Cl. Theoretical	% Decomposition
.0301 gms.	.0179	59.46	76.295	77.98
.0524 "	.0319	60.87	76.295	79.74
.0273 "	.0166	60.80	76.295	79.66

(2). The action of alcoholic sodium peroxide on perchloromethyl mercaptan.

(a) 5% sodium peroxide in a 15% alcoholic solution.

Fifty cubic centimeters of 5% Na_2O_2 in 15% alcohol(made by dissolving 10 grams of Na_2O_2 in 170 cc of water and 30 cc of 95% alcohol) were placed in a 500 cc bottle as in I (a) and (b) and the identical procedure carried out with results as follows:

Table V

Time	Sample of Perchloromethyl mercaptan	% Cl. Found	% Cl. Theoretical	% Decomposition
4 hours	.0408 gms.	45.37	76.295	59.44
Overnight	.0353 "	53.26	76.295	69.74
Overnight	.0575 "	48.87	76.295	64.03

(b) 20% sodium peroxide in a 15% alcoholic solution.

Fifty cubic centimeters of 20% Na_2O_2 in 15% alcohol (made by dissolving 40 grams Na_2O_2 in 170 of water and 30 cc. of 95% alcohol) were used as a decomposing agent, following the same method of that in 2 (a). Results:

Table VI.

Sample of Perchloromethyl Mercaptan	Grams Cl. found	% Cl. found	% Cl. Theoretical	% Decomposition
.0456 gms.	.0282	61.84	76.295	81.02
.0283 "	.0169	59.71	76.295	78.23
.0358 "	.0230	64.24	76.295	84.17

3. The action of potassium hydroxide on perchloromethyl mercaptan.

(a) 3% potassium hydroxide solution.

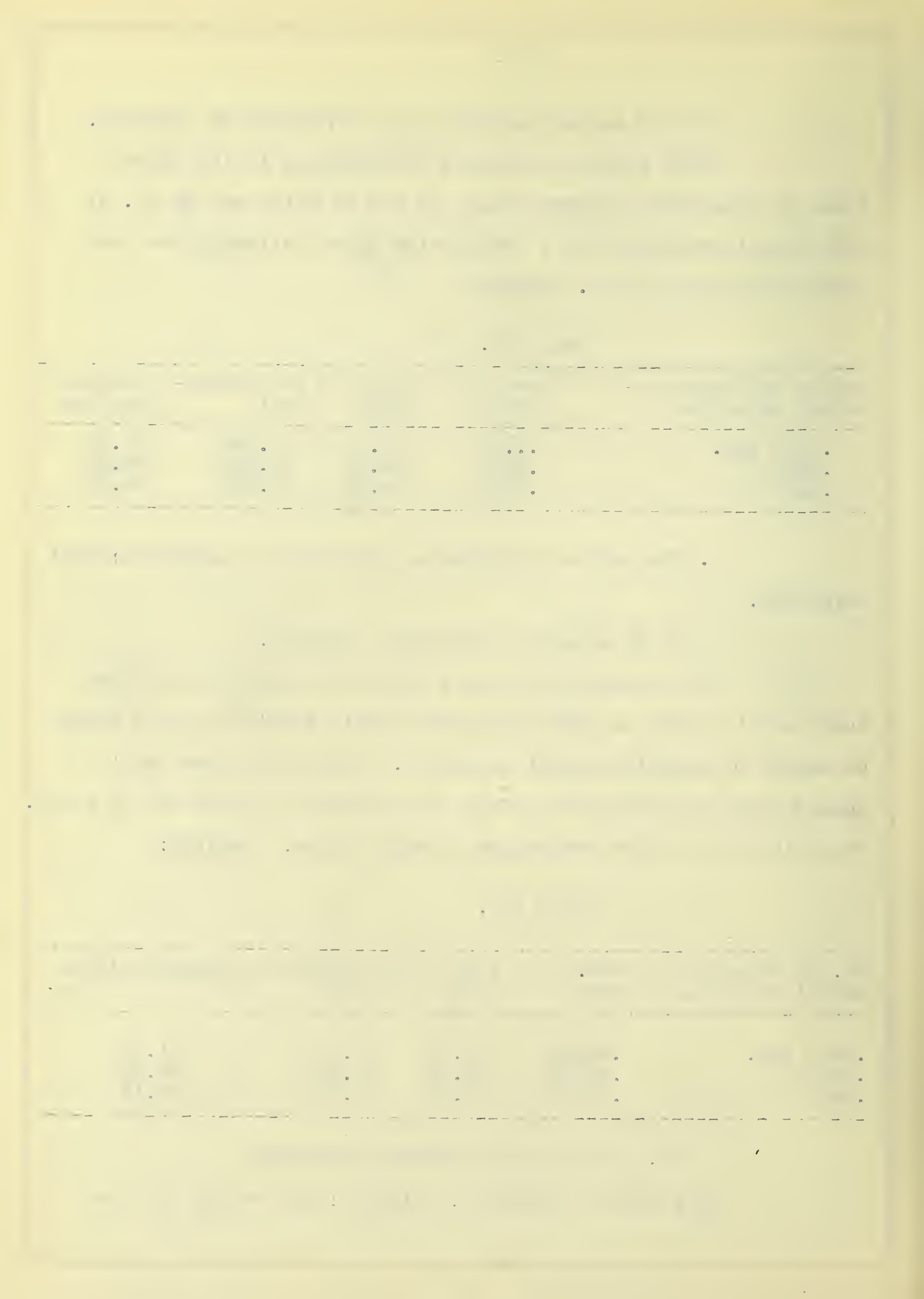
Fifty cubic centimeters of a 3% KOH aqueous solution were used in a 500 cc glass stoppered bottle together with a weighed sample of perchloromethyl mercaptan. The bottles were well shaken after the bulbs were broken and allowed to stand for 48 hours. The chlorine was then determined in each bottle. Results:

Table VII.

Wt. of Perchloromethyl mercaptan	Grms. Cl. found	% Cl. found	% Cl. Theoretical	% Decomposition
.0370 gms.	.01567	42.35	76.295	81.02
.0693 "	.02886	41.65	76.295	78.23
.0525 "	.01908	35.51	76.295	84.17

(b). 5% potassium hydroxide solution.

5% Potassium Hydroxide Solution: The method that was



used was identical to 3 (a) with a 5% K O H used instead of 3% K O H solution. Results:

Table VIII.

Grms. of Perchloromethyl mercaptan	Gms Cl. Found	% Cl. found	% Cl. Theoretical	% Decomposition
.0646	.02436	37.71	76.295	49.43
.0834	.03362	40.31	76.295	52.83
.0985	.04113	41.76	76.295	54.73

(B) In the following the vacuum bottle method was used:

(1) the action of alcoholic sodium hydroxide upon perchloromethyl mercaptan.

(a) 3% alcoholic sodium hydroxide solution.

Sixty cubic centimeters of a 3% solution of NaOH in 50% alcohol (3 grams of NaOH to 100 cc of 50% alc.) were drawn by means of the vacuum into a vacuum bottle of 2500 cc capacity, containing a weighed bulb of perchloromethyl mercaptan and a few glass beads to insure complete breakage of the bulb. After the bulb had been broken and the perchloromethyl mercaptan volatized, the bottle was well shaken and the pressure relieved before allowing to stand overnight. The next morning the contents of the bottle were carefully washed into a 500 cc Erlenmeyer flask, the alcohol evaporated off, using an air condensor, 10-15 cc of concentrated H N O_3 added (5 cc excess beyond neutrality) and the halogen precipitated with an excess $\frac{N}{10}$ Ag NO_3, and the excess determined with $\frac{N}{10}$ Na S CN. The percentage of chlorine found as compared to the theoretical percentage was taken as the indication of the

percentage of decomposition of the perchloromethyl mercaptan.

Results:

Table IX.

Wt. of Sample	Gms. Cl. Theoretical	Gms Cl. Found	% Cl. Found	% Decomposition
.0936 gms.	.0714	.0557	59.51	78.92
.1322 "	.1009	.0745	56.35	74.65

(b) 10% Alcoholic sodium hydroxide solution.

The method was identical to that described in B 1 (a). Ten grams of Na O H dissolved in 100 cc. of 50% alcohol was used as the decomposing agent. Results obtained:

Table X.

Wt. of Sample	Gms. Cl. Theoretical	Gms. Cl. Found	% Cl. Found	% Decomposition
.1204 gms.	.0919	.0732	60.79	80.56
.0973 "	.0742	.0570	58.58	77.66

V. SUMMARY

(1) A satisfactory method was developed for the determination of perchloromethyl mercaptan in low concentrations by the use ofaseven percent alcoholic sodium sulphite solution as the decomposing agent with subsequent determination of the chloride ion.

(2) The method gave accurate results in the hands of different observers previously unacquainted with the method.

(3) Alcoholic and aqueous solutions of sodium peroxide proved unsatisfactory by the direct decomposition method. Aqueous

potassium hydroxide was also found to be unsatisfactory. Likewise alcoholic sodium hydroxide proved to be unsuccessful in the vacuum bottle method of decomposition. None of these solutions gave quantitative results.

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