

QUANTITATIVE ANALYSIS OF THE MIXTURE OF GASES RESULTING FROM
THE PYROLYSIS OF METHYL CHLOROCARBONATE

by

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INTRODUCTION

In the investigations carried out at the University of Arizona concerning the thermal decomposition of chlorinated organic esters, one of the more difficult problems has proven to be the quantitative analysis of the resulting mixture of gases. Hardy /1/, in his investigation of the thermal decomposition of methyl chlorocarbonate, found that the ester decomposed into methyl chloride and carbon dioxide in the temperature range of 320 to 390°C. He analyzed for methyl chloride by burning the gas mixture resulting from the pyrolysis in a combustion pipet and measured the shrinkage in volume after absorption of the combustion products in potassium hydroxide solution. He then titrated the chloride ion in the absorbent. This method assumes that the sample analyzed consists only of methyl chloride and carbon dioxide. By this method the carbon dioxide was determined by difference and not directly. Such a procedure is always open to question. It was found that a direct determination of the carbon dioxide gravimetrically by absorption on Ascarite could not be made since methyl chloride was also absorbed. Yet, Yates /2/ successfully analyzed a mixture containing carbon dioxide and ethyl chloride by absorbing the former on Ascarite and later determining the ethyl chloride by a method as yet unreported in the literature. The difference in behavior of methyl chloride and ethyl chloride toward Ascarite is somewhat surprising. Curry /3/ determined carbon dioxide by the modified Winkler method as

described by Küster /4/ and Lindner /5/. The results of the analysis when applied to the decomposition products were not very consistent and cast some doubt on the procedure. Lashbrook /6/ determined carbon dioxide in a mixture of carbon dioxide and hydrogen chloride by taking both products up in barium hydroxide, back titrating the excess base with standard acid to determine the amount of both, acidifying the mixture and determining the chloride gravimetrically. The difference between the gravimetric determination and the titration gave the amount of carbon dioxide. The accuracy of this method is very doubtful because of the low concentration of barium ion. The literature dealing with the determination of carbon dioxide by absorption with barium hydroxide and the titration of the excess base to the phenolphthalein end point consistently shows that the titration must be carried out in the presence of excess barium ion. This excess cannot be supplied by the barium hydroxide as this requires too high a concentration of the base to permit an accurate determination of the base consumed in the absorption of carbon dioxide. Curry found that the addition of barium chloride gave better results but this makes the determination of chloride in the absorbent impossible. She also found that barium nitrate did not meet the requirements set forth in the literature. Both Lashbrook and Curry determined the amount of ethyl chloride by difference.

In summary, Hardy determined the amount of alkyl halide present directly and the carbon dioxide by difference while Lashbrook and Curry determined the carbon dioxide directly and the alkyl halide by difference. The method employed by Lashbrook is questionable and that employed by Curry did not give very good results.

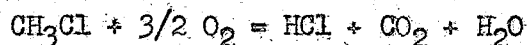
Yates determined ethyl chloride by mixing it with the stoichiometric ratio of oxygen, exploding the mixture by passing a spark through it, absorbing the hydrogen chloride produced in sodium hydroxide and titrating the chloride ion. This method appeared very promising as it is much simpler and quicker than anything reported in the literature. However, the amount of experimental work done on known mixtures using this method was far from sufficient to adopt it without further careful investigation. A part of this thesis reports a study of the accuracy of the determination of methyl chloride by this method, with the object of determining the best procedure to be followed in the analysis. In addition, the accuracy of the determination of carbon dioxide by absorption in barium hydroxide was investigated, and a method sought for the determination of methyl chloride and carbon dioxide in a mixture without resorting to a determination by difference.

QUANTITATIVE DETERMINATION OF METHYL CHLORIDE

Explosion Method

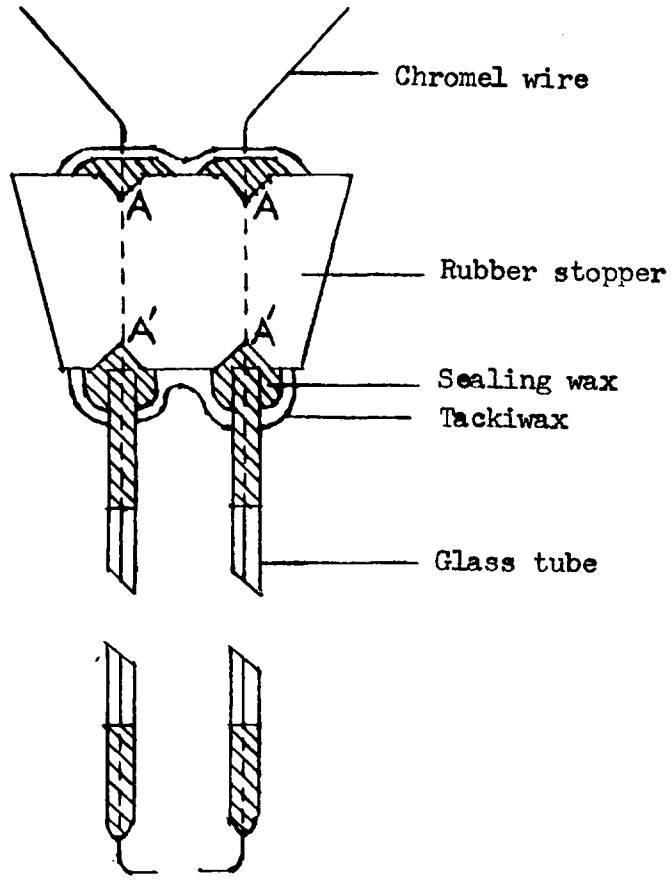
Experimental:

Methyl chloride was found to be combustible in air. It could be ignited with a Bunsen flame and burned in air giving a self-sustaining flame of several seconds duration. The reaction for the combustion is expressed by the following equation:



The explosion method first described by Yates /2/ for the determination of ethyl chloride consisted of mixing a measured volume of ethyl chloride with three times its volume of oxygen and exploding the mixture by passing a spark through it. In applying this method to methyl chloride, a volume of oxygen one and one-half that of methyl chloride was used. The hydrogen chloride produced was then absorbed in an excess of sodium hydroxide, neutralized, and the solution titrated for chloride ion. Yates gives no directions for the construction of the sparking device he used so it is not known how the one used in this work compares with his. After some experimentation the device adopted was the one shown in Figure 1. Two holes were burned through a solid rubber stopper with a hot wire and depressions burned with a glass rod at the entrance and exit of these holes (points A and A'). Appropriate lengths of Chromel-A wire, size 18, were then forced through the holes. Sealing wax was carefully worked around the wires

Figure 1
Spark-plug



with a hot spatula to fill the depressions and form a tight seal. An excess of the wax was built up around the wires on the under side of the stopper (points A^r). The ends of appropriate lengths of small diameter glass tubing were heated until the hole remaining just permitted the wire to pass through it. This portion of the tubes was filled with small pieces of sealing wax to a depth of one-half inch. The wires were heated along with the open ends of the glass tubing and the tubing slipped over the wires and firmly embedded in the wax at the base of the stopper. The wax was worked with a hot spatula until a tight seal was formed. The ends of the wires were bent to form a spark gap of about three millimeters. Both upper and lower surfaces of the stopper were coated with Cenco Softseal Tackiwax. This arrangement was found to be completely air tight and washings of the lower surface of the stopper were shown to be chloride free. The lengths of the wire and of the tubing were chosen so that the electrodes extended about one inch into the body of a one liter, three neck, Pyrex flask when placed in the center neck. The spark was produced by attaching one of the wires to the ground and touching a Tesla coil to the other wire. One of the other necks was fitted with a rubber stopper holding a capillary stopcock tied in with a rubber saddle /7/. The remaining neck was sealed with a solid rubber stopper. The flask was evacuated and the gas samples and sodium hydroxide solution introduced through this stopcock. All three stoppers were sealed by coating the joints with Cenco Softseal Tackiwax.

Gas samples were measured out by means of a 100 ml. gas buret calibrated to read 0.2 ml. The outlet tube of the gas buret was connected to a T-tube by means of a short length of rubber tubing. The side arm

of the T-tube lead to a glass stopcock and then to the cylinder of methyl chloride or to the oxygen tank depending upon which gas was being used. The stopcock was added to guard against any leakage of the valve on the cylinder of gas or around the tubing connections to the cylinder. The other arm of the T-tube lead to the explosion flask.

The tubing connections between the explosion flask, the cylinder of gas, and the gas buret were evacuated by using the gas buret as a Topley pump. The connections and buret were rinsed out several times with small portions of the gas to be added to the flask. The gas buret was then filled with the gas to be added and the stopcock between the gas cylinder and the T-tube closed. During the operation of filling the gas buret a slight pressure was always maintained on the gas so that any leakage would be outward and not inward to prevent contamination of the sample. The barometric pressure and temperature were recorded along with the volume reading. The sample was drawn into the previously evacuated explosion flask by opening the stopcock of the explosion flask. The volume of the gas remaining in the buret was recorded. The difference in volumes gave the size of the sample.

The mixture of gases was exploded and 25 ml. of approximately 0.1 N sodium hydroxide solution was then drawn into the flask through the capillary stopcock. Yates exploded samples of about 0.45 millimoles of ethyl chloride and absorbed the products with 50 ml. of approximately 0.15 N sodium hydroxide solution which corresponds to 7.5 millimoles of base. In the work with methyl chloride the largest sample of methyl chloride taken was 2.35 millimoles and the base used contained at the very least 2.5 millimoles of sodium hydroxide. In all cases the

resulting solution was found to be basic. Yates gives no reason for using such an excess of sodium hydroxide. The amount of base was purposely kept low in the work with methyl chloride to avoid introducing any chloride ion from the sodium hydroxide and from the nitric acid used in the subsequent neutralization. Also, the amount of salt present has a very marked effect upon the end point of the titration. The higher the concentration of electrolytes in the solution to be titrated the less precise the results. The small quantity of sodium hydroxide reduced the amount of sodium nitrate formed.

The sodium hydroxide was shaken in the flask, care being taken to coat the sides of the flask and the electrodes with the solution. The minimum period of contact of the base with the products was twenty minutes. Air was admitted to the flask, the seal about the solid rubber stopper broken, the Tackiwax carefully wiped away, and the contents added to a 250 ml. Erlenmeyer flask. The explosion flask was rinsed out four times with distilled water and the washings added to the flask to give a final volume of 100 to 130 ml. The pH of the solution was adjusted to 4 to 6 by adding 0.2 N nitric acid and following the neutralization with Fischer Alkacid test paper. The solution was titrated with 0.05 N silver nitrate solution using a 50 ml. buret. Six to eight drops of a 0.1 per cent solution of dichlorofluorescein in 70 per cent ethyl alcohol were used as the indicator. The end point is the formation of a salmon pink color in the solution and precipitate.

The silver nitrate was standardized against Merck Reagent Grade sodium chloride dried at 110°C for two hours and cooled for one hour. The sodium chloride was weighed into a 250 ml. volumetric flask

which had previously been calibrated against a 50 ml. pipet for aliquot portions. From three to four titrations were made for each weighing. Table 1 gives the average deviation from the mean for the various standardizations of the two solutions of silver nitrate used in the course of the investigation. It is of interest as it indicates the precision of the titration. However, it must be remembered that the solution titrated was neutral and had no excess electrolyte present.

Table 1

Average Deviation from the Mean in the Standardization
of the Silver Nitrate Solution

Solution	Trial	Number of titrations	Average Deviation from the mean in parts per thousand
I	1	4	0.92
	2	3	0.69
II	1	4	0.65
	2	4	0.57
	3	3	0.63
	4*	4	0.61
	5*	4	0.87

*These standardizations were carried out with 5 ml. of a 2 per cent dextrin solution added.

The weighted deviation from the mean is 0.71 parts per thousand. This indicates a high degree of precision for the titration. The standardizations were carried out at different times during the investigation. The normalities obtained showed no significant variation indicating that the end point was reproducible and that no chloride was introduced by the addition of dextrin. The reason for this addition will be stated later.

Kolthoff, Lauer, and Sunde /8/ state that for satisfactory

results it is sufficient to adjust the acidity before titration so that the solution is slightly acid to phenolphthalein. The pH should not be less than 4. Preliminary work showed that phenolphthalein is not a suitable indicator as the carbon dioxide causes the color to fade and the acidity cannot be adjusted with any degree of accuracy. The dichlorofluorescein indicator is a weak acid and its action depends upon the presence of dichlorofluoresceinate ions. At a pH less than 4 the ionization of the indicator is suppressed to such an extent that it no longer functions. The Alkacid test paper is far more reliable in adjusting the acidity.

The dichlorofluoresceinate ions are adsorbed on the surface of the precipitate in the presence of excess silver to form a pink color. Because of this adsorption, coagulation of the precipitate must be avoided because the coagulated precipitate removes the indicator and makes the end point difficult to detect. Coagulation is increased by the presence of ions of other electrolytes and such a situation exists when the excess base is neutralized with nitric acid. During the preliminary investigation blanks were run on the reagents by first titrating a definite volume of a solution of sodium chloride and then titrating a solution containing the same volume of sodium chloride but with a definite amount of the 0.1 N sodium hydroxide solution added to it and neutralized to be slightly acid to phenolphthalein with 0.2 N nitric acid. The end point became very poor and the deviation from the mean increased as greater amounts of sodium hydroxide were used. To prevent coagulation 5 ml. of a 2 per cent solution of dextrin were added. Table 2 summarizes the results of the effect of the dextrin on the precision. To prevent coagulation, five milliliters of dextrin

Table 2

The Effect of Dextrin on the Precision of the Titration of Sodium Chloride in the Presence of Varying Amounts of Sodium Nitrate

Amount of 0.1 N NaOH solution added and neutralized with HNO ₃ (ml.)	Average deviation from the mean in parts per thousand	
	Without dextrin	With dextrin
20	5.00	1.18
40	29.98	0.99

solution were added to the solution containing the products of the combustion in the actual analyses.

The end point for the titration is very sensitive to light and changes from a salmon pink to a dark reddish purple in a matter of minutes even in diffuse light. In order to obtain satisfactory results, the titration should be carried to completion as rapidly as possible once the end point is approached.

With these precautions in mind, 20 ml. of approximately 0.09 N sodium chloride solution and 25 ml. of 0.1 N sodium hydroxide solution were mixed, diluted to 100 ml., two drops of phenolphthalein indicator added, and the solution neutralized with nitric acid until slightly acid to phenolphthalein. Fischer Alkacid test paper showed the pH to be from 5 to 6. Five milliliters of the dextrin solution were added and the solution titrated using six drops of dichlorofluorescein indicator. The results of five trials are shown in Table 3. The quantity of chloride found when the same quantity of sodium chloride was titrated with dextrin present but without the addition of any

Table 3

Titration of the Reagents Using Dextrin Solution With a
Constant Quantity of Sodium Chloride Present

Trial	Millimoles of chloride found	Deviation from the mean in parts per thousand
1	1.863	1.08
2	1.863	1.08
3	1.860	0.55
4	1.859	1.08
5	1.862	0.55
Mean	1.861	0.87

sodium hydroxide or nitric acid was 1.862 millimoles on the basis of four titrations. This indicates that the chloride introduced by the reagents was negligible. The standardizations showed the dextrin to be chloride free.

When actual analyses of methyl chloride samples were undertaken it was found more convenient to run a series of explosions and save the solutions to be titrated as a group. The results are divided into series on this basis. The last series, Series E, was made in such a manner that the temperature of the gases at the time of explosion was varied in order to determine whether the explosion would be affected by the temperature. After the gases were added to the explosion flask, the flask was clamped in a crock filled with water. The water was stirred by means of an air stirrer and the temperature measured by a thermometer calibrated to 0.1°C. The water was either cooled by adding ice or heated by bubbling steam through it. A rubber stopper holding a similar thermometer was substituted for the solid rubber stopper in

the explosion flask. As soon as the temperature of the thermostat and the gases in the flask were within a few tenths of a degree of one another, the explosion was initiated.

During the course of the investigation it was found that several of the gas mixtures did not explode. It was thought that this might be because the pressure of the gases in the flask was too low. In order to test this a gas storage bulb containing a mixture of methyl chloride and oxygen was connected to one neck of the explosion flask and a manometer to the other. The flask was evacuated and small samples of the mixture added to the flask, pressure readings being taken directly. After each addition, the manometer was cut off from the flask by means of a stopcock and a spark passed through the mixture. On the basis of two trials with two different mixtures, the minimum pressure for an explosion was found to be 52 mm. of mercury total pressure in the flask. Since all of the explosions that failed were above this pressure the failure was not because of insufficient pressure.

A calculation of the number of millimoles of gas in a 50 ml. sample was carried out by the van der Waals equation, the ideal gas equation, and the Berthelot equation assuming the pressure to be 700 mm. and the temperature to be 25°C. The Berthelot equation and the van der Waals equation were solved for the volume of one mole of the gas at these conditions. The number of millimoles in the sample was then found by dividing the actual volume taken by the volume of one mole. The van der Waals equation gave 1.8997 millimoles, the Berthelot equation gave 1.9099 millimoles and the ideal gas equation gave 1.8819 millimoles. Assuming the van der Waals equation to be correct,

the Berthelot equation gives results that are 0.53 per cent high while the ideal gas equation gives results that 0.94 per cent low. Since the van der Waals equation is too difficult to solve for practical purposes because it is a cubic equation in terms of volume, the Berthelot equation was used to calculate the number of millimoles in the sample because it gave a smaller error than the ideal gas equation.

Results:

The results of analyses by the explosion method are given in Table 4. The explosions are arranged in the order in which they were made, a Series being a group of consecutive titrations of the products. The various column headings give the following information:

Millim³ CH₃Cl taken - the number of millimoles of methyl chloride in the sample as calculated from the Berthelot equation.

Vol. O₂/Vol. CH₃Cl - the ratio of the volume of oxygen to that of the methyl chloride.

Pressure - the total pressure in the flask at the time of explosion in millimeters of mercury, that is, the sum of the partial pressure of residual air due to incomplete evacuation (at the most this was three millimeters) and the partial pressure of the mixture added, as computed by Boyle's and Charles' laws.

Period of contact - the period of contact of the sodium hydroxide solution with the products of the explosion in minutes.

Temp. - the temperature of the gases at the time of explosion in degrees Centigrade.

% error - the percentage error which was computed by taking the difference between the number of millimoles of chloride found and the

number of millimoles of gas calculated, dividing by the latter, and multiplying by 100. If the results were high, the percentage error is preceded by a plus sign and if they were low, the error is preceded by a minus sign.

NE denotes that no explosion took place and NE* denotes that the electrodes were found to be coated or corroded and the failure of the explosion is thought to be due to the poor spark produced because of this coating.

Table 4
Results of Analyses

Trial	Millim. CH ₂ Cl taken	Vol. O ₂ Vol. CH ₃ Cl	Pressure mm.	Period of contact min.	Temp.	% error
Series A						
1	1.893	1.63	84.3	20	25.1	+ 2.58
2	1.979	1.53	85.5	20	27.9	+ 0.15
3	1.968	1.48	83.0	30	27.2	- 3.35
4	2.007	1.39	81.3	20	24.7	- 3.44
5	2.186	1.51	91.9	30	23.6	- 5.26
Series B						
6	1.970	1.54	85.1	---	26.6	- 5.03
7	---	1.53	80.2	---	23.1	NE*
8	1.906	1.54	81.9	---	25.8	- 3.88
9	1.949	1.52	82.9	---	24.6	- 5.95
10	1.960	1.61	85.5	---	21.2	- 4.84
11	2.034	1.53	86.1	---	22.5	- 6.24
12	1.960	1.51	83.9	---	26.7	- 4.80
13	2.362	1.53	100.7	---	26.3	- 6.18
Series C						
14	2.353	1.55	101.2	---	27.9	- 3.91
15	2.058	1.57	90.4	---	29.1	- 4.13
16	1.827	1.52	79.4	---	29.4	- 5.15
17	---	1.52	72.7	---	28.2	NE*
18	1.763	1.54	77.3	---	29.4	- 3.97
19	---	1.52	72.5	---	29.8	NE

Table 4 continued

Trial	Millim. CH ₂ Cl taken	Vol. O ₂ Vol. CH ₂ Cl	Pressure mm.	Period of contact min.	Temp.	% error
Series D						
20	2.329	1.54	100.8	35	29.0	- 3.65
21	2.229	1.53	97.1	30	31.3	- 3.73
22	2.201	1.58	96.6	35	28.6	- 3.68
23	2.200	1.55	96.2	50	30.6	- 3.50
24	2.008	1.52	87.1	45	30.2	- 1.54
25	2.321	1.53	99.8	60	28.5	- 2.80
26	2.350	1.52	101.6	60	31.0	- 4.47
27	2.176	1.61	97.6	70	30.8	- 2.85
28	1.941	1.53	84.3	60	29.6	- 2.16
Series E						
29	2.216	1.58	93.4	40	15.1	- 1.08
30	2.199	1.60	93.4	40	15.2	- 2.18
31	2.021	1.54	84.3	40	15.1	- 2.52
32	2.136	1.52	89.1	60	18.0	- 2.62
33	2.057	1.54	87.2	35	20.0	- 3.01
34	2.247	1.50	94.0	30	21.9	- 2.45
35	2.046	1.56	88.9	45	25.0	- 2.35
36	2.113	1.64	95.2	40	28.0	- 2.98
37	1.956	1.54	85.7	45	30.0	- 2.51
38	2.092	1.53	92.6	45	35.0	- 2.87
39	2.210	1.50	96.6	65	35.0	- 2.04
40	2.060	1.55	93.5	40	40.1	- 2.67
41	2.190	1.55	98.9	40	40.0	- 3.11
42	2.288	1.57	105.8	80	44.9	2.14
43	2.022	1.54	91.0	40	45.0	- 2.52
44	2.061	1.52	95.4	195	50.5	- 0.58
45	1.973	1.54	90.4	145	50.1	- 2.38

Treatment of Results:

The various statistical measures referred to in this section are taken from Hoel /9/.

The mean and standard deviation cannot be computed from the absolute values of the error because of the positive and negative values involved, that is, if the absolute value were used, the error of + 2.58 per cent would have the same significance as an error of - 2.58 per-cent.

and any conclusions reached would be false. Therefore a - 3 was added to each percentage error and the results multiplied by -1.1. The result of the computation of the mean was then changed back by subtracting three from the result and multiplying this value by - 1. Using this method, the mean error, m , for the forty-two successful explosions is - 3.15 per cent and the standard deviation, s , is 1.65 per cent. If it is assumed that the sample investigated comes from a normal population, then $m \pm 2s$ includes the values from + 0.15 per cent to - 6.45 per cent. This may be interpreted as meaning that 95 per cent of the data may be expected to lie between these limits. Similarly, 99.7 per cent of the data may be expected to lie in the range of $m \pm 3s$ or between + 1.80 per cent and - 8.10 per cent. Explosion 1 shows an error of + 2.58 per cent which lies well outside the $m \pm 3s$ limits. Therefore, the probability of attaining such a result from a random sample is less than one chance in 200. This indicates that the error is more likely to be due to a definite cause instead of resulting from randomness of sampling and may be discarded with some degree of safety. If this result is omitted the new mean becomes - 3.29 per cent and the new standard deviation 1.41 per cent. The new limits for $m \pm 2s$ become - 0.47 per cent and - 6.11 per cent; the new limits for $m \pm 3s$ become + 0.94 per cent and - 7.52 per cent. Some of the remaining results lie outside the $m \pm 2s$ range but not outside the $m \pm 3s$ range. Therefore they were not discarded as five per cent of the data may be expected to do this. Therefore, in this method of analysis, the mean error is - 3.29 per cent and 95 per cent of the results may be expected to fall in the range of - 0.47 per cent to - 6.11 per cent. This would indicate that the method is neither very accurate nor precise.

The next statistical measure applied was the linear correlation coefficient, r . It was used in preference to the curvilinear correlation coefficient as the scatter diagrams of the percentage error plotted against the various variables considered, namely, the millimoles of methyl chloride taken, the ratio of the volume of oxygen to methyl chloride, the pressure in the flask at the time of explosion, the period of contact of the base with the products, and the temperature at the time of explosion did not show any particular trend towards a curve. The correlation coefficient may be interpreted as follows: If a least-squares line or regression line is fitted to the data considered and the line passes through all points plotted then r^2 is unity and the fit is 100 per cent ($= r^2 \times 100$). However, if the data are such that if a plot of one variable against the other gives merely a cloud of points such that a regression line drawn in any position fits the data equally well, then r^2 approaches zero. The results of computing the linear correlation coefficient for unclassified data considering the percentage error as a function of the various variables are as follows:

Millimoles of methyl chloride taken:

$r^2 = 0.0033$ or 0.33 per cent. This indicates no significant relationship of the percentage error to the size of the sample taken in the range of 1.76 to 2.36 millimoles. This is to be expected as the percentage error should be independent of the size of the sample except for a wide range of sample sizes.

Ratio of the volume of oxygen to that of methyl chloride:

$r^2 = 0.0385$ or 3.85 per cent. This indicates no significant relationship of the percentage error to the ratio of the volumes of the

gases in the range of 1.39 to 1.64. Thus the ratio of the volumes does not appear to be a critical factor. However, if the ratio drops too low, incomplete combustion may be expected and a much greater error should result. This apparently was not encountered in this investigation. Pressure in the flask at the time of explosion:

$r^2 = 0.0253$ or 2.53 per cent. There is no significant relationship of the percentage error to the pressure in the flask in the range of 77.3 to 101.6 millimeters. It was thought at one time that the pressure might determine the propagation of the explosion through the flask.

The time of contact of the 0.1 N sodium hydroxide solution with the products of the explosion:

$r^2 = 0.1165$ or 11.65 per cent. The relationship is somewhat stronger but is still quite small. In order to investigate this more fully, the percentage error was arranged with regard to the period of contact. The results are shown in Table 5. This indicates that the error is almost constant with varying periods of contact in the range of 20 to 195 minutes.

The temperature of the gases in the flask at the time of explosion:

$r^2 = 0.3682$ or 36.82 per cent. This is the highest value of the correlation coefficient yet obtained. However, Series E was made with temperature as the specific variable and it shows the error to be independent of the temperature in the range of 15°C to 50°C.

The last statistical measure was a test for the randomness of sequence. If the errors having an algebraic value greater than the mean error are assigned a value A and those with an algebraic value less than the mean error the letter B then the sequence is:

Table 5

The Percentage Error for Various Periods of Contact
of the Base with the Products of Combustion

Period of contact (min.)	Trial	Percentage error	
30	3	- 3.35	
	5	- 5.26	
	21	- 3.73	
	34	- 2.45	
	Mean		- 3.70
35	20	- 3.65	
	22	- 3.68	
	33	- 3.01	
	Mean		- 3.45
40	29	- 1.08	
	30	- 2.18	
	31	- 2.52	
	36	- 2.98	
	40	- 2.67	
	41	- 3.11	
	43	- 2.52	
	Mean		- 2.44
45	24	- 1.54	
	35	- 2.35	
	37	- 2.51	
	38	- 2.87	
	Mean		- 2.32
60	25	- 2.80	
	26	- 4.47	
	28	- 2.16	
	32	- 2.62	
	Mean		- 3.01
70	27	- 2.85	
80	42	- 2.14	
145	45	- 2.38	

1 A -- 18 B's -- 2 A's -- 1 B -- 19 A's

There are three runs of A's and two runs of B's or a total of five runs. There are twenty-two A's and nineteen B's. If it is assumed that the number of A's equals the number of B's (=20) then according to the table in Hoel, the total number of runs at the 2.5 per cent significance level has a minimum value of fourteen. The conclusion is that the probability of obtaining this sequence is much less than 2.5 chances out of 100. This indicates that the sequence is not at all random. Table 6 gives the mean value of the error for the various series.

Table 6

Mean Error for the Various Series

Series	Mean Percentage Error
A	- 2.98
B	- 5.27
C	- 4.29
D	- 3.15
E	- 2.35

The results within any series appear to be random but there is a marked trend towards a decreasing error from series to series. No explanation for this is offered at this time. The standardizations of the silver nitrate were carried out at different times and were in close agreement so that it does not appear to be a matter of the standard solution changing in concentration nor a matter of indicator error. If the titrations had been carried out in such a way that the various Series were titrated to a different color, this should have also been the case in the standardizations. The standards were also arranged so that the concentration of chloride ion in the standard

was of the same magnitude as the concentration in the solutions resulting from the explosions.

Combustion Analysis

No final conclusion about the accuracy of the explosion method could be made until the purity of the methyl chloride used could be established by some independent method of analysis. The combustion method of Martinek and Marti /10/ was modified to fit the apparatus available and adapted to a semi-micro scale rather than a micro scale.

Experimental:

A gas pipet was constructed consisting of a capillary tube sealed to each end of a tube 1.6 cm. in outside diameter and 11 cm. long. Calibration marks were placed on the capillary tubing and the volume between the marks found from the weight of water that could be held between the two calibrations and the density of the water at the temperature at which the calibration was made. Three independent calibrations gave a mean volume of 16.75 ± 0.01 ml. A two-way stopcock was attached to the top of the pipet so that the gas samples could be drawn into the pipet through one tube and then admitted to the stream of air going to the combustion tube through the other. Air was drawn through the furnace by means of a water pump. It was first passed over calcium chloride and soda lime and then drawn into a bulb attached to the outlet tube of the gas pipet where the methyl chloride was mixed with it. The methyl chloride was driven into this bulb by regulating the flow of mercury into the pipet by means of a screw clamp fastened to the rubber tubing leading from the mercury leveling

bulb to the pipet. The mixture of methyl chloride and air was passed into a Vycoor combustion tube 55 cm. in length with an inside diameter of 1.3 cm. The tube was heated by means of an electric resistance furnace of 33 cm. outside length. This gave a somewhat shorter arrangement than used by Martinek and Marti. The products of the combustion were then passed into two gas absorption tubes in series through sintered-glass bubbler tubes. The absorption tubes were about 11 cm. high. The last tube was connected to a safety bottle and another bottle filled with water which was attached to the water pump. The bottle of water was used to estimate the rate of flow of gas through the system by observing the rate at which air, after passing through the combustion train, bubbled through it. Martinek and Marti took one hour to burn 5 ml. of gas at a temperature of 1000°C . with a rate of flow of 0.5 cubic feet per hour. The furnace used in this work attained a temperature of 950°C in one and one-half hours with no resistance on a variable resistor in series with it. This was considered to be about the maximum temperature possible. A rate of flow of 0.5 cubic feet per hour was found to be much too fast as the gases were not heated sufficiently because of the shorter furnace and the lower temperature. Therefore the rate of flow was arbitrarily adjusted so that the rate of bubbling through the bottle filled with water was just past the point where the individual bubbles could be counted.

Three hours were taken to burn the sample.

The hydrogen chloride formed by the combustion was taken up in 40 ml. of a one per cent solution of sodium carbonate saturated with arsenious oxide which had been filtered to remove the excess of the oxide. After the combustion this solution was carefully washed into a

100 ml. volumetric flask previously calibrated against a 25 ml. pipet. Three washings of the absorption apparatus were made using no more than 30 ml. of water for the operation and the washings added to the flask. At the same time, 40 ml. of the absorbent were placed in another 100 ml. volumetric flask calibrated against the same pipet. This second solution served as a blank. Five milliliters of three to one nitric acid solution were added to each flask to neutralize the carbonate, exactly 25 ml. of approximately 0.026 N silver nitrate solution added to each flask and the solution diluted to the calibration on the flask. This volume of silver nitrate solution furnished an excess of silver ion. The solutions were then filtered through dry sintered-glass filtering crucibles into perfectly dry filtering flasks to remove the silver chloride. The filtering apparatus was all glass. The pipet used in the calibration of the volumetric flasks was used to withdraw three samples from the determination and from the blank for titration. The solutions were titrated for the excess silver ion in 100 ml. Erlenmeyer flasks with a 10 ml. micro buret calibrated to read 0.05 ml. with 0.021 N potassium thiocyanate solution using 10 drops of a 50 per cent saturated solution of ferric ammonium sulfate solution as the indicator. In the analyses the sample was titrated and a blank titrated immediately afterward to the same color. The difference in volumes used for the determination and for the blank multiplied by the normality of the thiocyanate solution gave the millimoles of chloride ion in the determination. This procedure has advantages in that the exact concentration of the silver nitrated solution was not needed, the indicator error was reduced to a minimum, and no error was introduced by chloride in the reagents.

In this and all other titrations following the volumes of the titrating solutions were corrected to 20°C.

The potassium thiocyanate was standardized against silver nitrate as a primary standard. The silver nitrate was purified by dissolving it in 3N nitric acid and filtering it in an all glass system to remove dust and lint. The solution was concentrated to the saturation point on a steam bath, the silver nitrate allowed to crystallize and the crystals collected on a sintered-glass filtering crucible. The crystals were dried at 110°C for one hour, placed in a porcelain crucible and heated in a sand bath to above the melting point for ten minutes. On cooling, the silver nitrate was broken up and placed in a weighing bottle. The product was perfectly clear and showed no discoloration. The silver nitrate was weighed into a 100 ml. volumetric flask previously calibrated against a 20 ml. pipet. Samples were taken with this pipet, acidified with 5 ml. of 6 N nitric acid and titrated in a 100 ml. Erlenmeyer flask with the potassium thiocyanate solution using a 50 ml. buret. Ten drops of indicator were used. An indicator blank of distilled water and 5 ml. of acid was run with each titration. Barium sulfate was added to serve as a background in observing the color. Two separate weighings were made and three titrations made of each sample weighed. The deviation from the overall mean was 0.83 parts per thousand showing a good degree of precision.

Results:

Two cylinders of methyl chloride were available. Cylinder 2 was the one from which the methyl chloride was taken for the work on the explosions. The results of the analyses are shown in Table 7. As before, the size of the sample was calculated from the Berthelot equation.

Table 7

Results of the Combustion of Methyl Chloride

Combustion	Millim. CH ₂ Cl taken	Millim. found (mean value)	Number of titrations	Aver. Deviation from the mean (parts/1000)	% error
Gas cylinder 1					
1	0.6198	0.6187	2	4.5	- 0.18
2	0.6248	0.6160	3	4.2	- 1.41
3	0.6230	0.6233	3	2.1	- 0.05
4	0.6202	0.6172	3	1.6	- 0.48
Gas cylinder 2					
1	0.6266	0.6198	3	5.7	- 1.09
2	0.6295	0.6312	3	4.0	+ 0.27
3	0.6297	0.6323	3	0.7	+ 0.41
4	0.6297	0.6298	3	4.1	+ 0.02
5	0.6288	0.6344	3	5.7	+ 0.89

Treatment of Results:

For gas cylinder 1, combustion 2 shows an error somewhat larger than usual. The method is subject to loss of chloride in poor washing technique so that the omission of results showing a large error seems justified especially if the error is negative. On the basis of combustions 1, 3, and 4 the mean error is - 0.24 per cent. For gas cylinder 2, combustion 1 may be omitted for the same reason making the mean error + 0.40 per cent.

The precision is much poorer than in the standardization. This is probably indicator error. The quantity of precipitate formed in the blank is quite a bit more than in the determination which changes the background against which the colors are matched and this may be the source of error.

These analyses indicate that the methyl chloride is within

0.5 per cent of being pure and the deviations resulting from the explosion technique cannot be explained by the impurity of the methyl chloride.

QUANTITATIVE DETERMINATION OF CARBON DIOXIDE

A search of the literature showed that one of the more successful volumetric determinations of carbon dioxide is the absorption of the gas in standard barium hydroxide solution with barium chloride added and the titration of this solution with standard hydrochloric acid to a very faint pink using phenolphthalein as the indicator. This is a modification of the original Winkler method /4/ /5/. Kolthoff and Stenger /11/ recommend a barium ion concentration of 0.1 N at the end point. Truog /12/ used four drops of a one per cent solution of phenolphthalein in 95 per cent ethyl alcohol for a titration where the final volume was 200 ml.

Carbonate free distilled water was siphoned into a carboy that had been rinsed with ethyl alcohol and dried by passing carbon dioxide free air through it. The carbon dioxide free air was produced by forcing compressed air through a concentrated solution of sodium hydroxide, a tower containing soda lime, and finally through a calcium chloride tube containing Ascarite. An 0.04 N solution of hydrochloric acid was prepared from some of this water and stored in a stock bottle previously rinsed with alcohol vapors. The stock bottle was attached by means of glass tubing to a 50 ml. buret equipped with a two-way stopcock which permitted the buret to be filled from the bottom. The acid was pumped into the buret by means of a rubber hand bulb, the latter being attached to a drying tube containing Ascarite so that

carbon dioxide was removed from the air pumped into the stock bottle. The top of the buret was also equipped with a drying tube of Ascarite. In this way, the solution was completely protected from the carbon dioxide in the air.

A solution of barium hydroxide containing barium was prepared so that the concentration of the base was 0.05 N and the concentration of the barium chloride was such that if 50 ml. of the solution were taken and diluted to 200 ml. the final concentration of barium chloride was 0.1 N. This would be 0.4 N with respect to barium chloride in the stock solution. The reagents were mixed in a six liter flask protected by a soda lime tube and the barium carbonate allowed to precipitate. The amount of barium carbonate was appreciable as the solid barium hydroxide was quite old and contaminated with carbonate. This was filtered directly into a paraffin coated stock bottle by means of a Büchner funnel using a double layer of filter paper. During the filtration the funnel was never allowed to empty completely to prevent air from entering the bottle. The stock bottle containing the base was connected to the same type of buret as that used for the acid. When not in use, the tip of the buret containing the base was protected from the carbon dioxide in the air by immersing it in a test tube of distilled water.

The acid was standardized against Merck Reagent Grade sodium carbonate dried at 110°C for two hours. A few drops of a 0.1 per cent solution of methyl red in 95 per cent ethyl alcohol were used as the indicator. On nearing the end point, the carbon dioxide was boiled out of the solution and the titration continued with the solution hot. On the basis of three weighings and four titrations for each weighing,

the average deviation from the mean was 0.96 parts per thousand.

Samples of the barium hydroxide solution diluted to 150 ml. were titrated with the acid to a very faint pink using 4 drops of phenolphthalein indicator in the presence of added barium sulfate which gave a white suspension similar to that encountered in the titration of carbonate samples. The titration was carried out in a 500 ml. flask equipped with a two-hole rubber stopper. A glass tube projected through one hole to a point just above the surface of the liquid and carbon dioxide free air was forced through this tube. The tip of the acid buret projected into the flask through the other hole. Before addition of the base to the flask, the flask was rinsed out with alcohol and dried by forcing carbon dioxide free air through it. The flask was kept stoppered as much as possible. On the basis of eleven titrations the mean normality was found to be 0.05043 and the average deviation from the mean was 1.32 parts per thousand. The greater deviation is to be expected due to the inability to split drops using the rather cumbersome arrangement to protect against carbon dioxide.

Samples of sodium carbonate were weighed into a 250 ml. volumetric flask, dissolved in carbonate free water, and one-fifth taken and pipeted into a flask rinsed out with alcohol vapors. The pipet was protected from the breath by means of a drying tube filled with Ascarite. A measured volume of the barium hydroxide solution was added to this, the solution diluted to 150 ml. and titrated with the acid. Since this did not involve the addition of any base or acid to the solution and all the carbonate was precipitated before the titration, the same amount of acid should have been required to neutralize the base as in the standardization of the barium hydroxide solution. Table 8

indicates that more acid was required than calculated from the volume of the base taken. The last column indicates the number of millimoles of carbon dioxide corresponding to this difference in the volumes of acid. This is interpreted as indicating that some of the barium carbonate

Table 8

Results of Titrating Barium Hydroxide
in the Presence of Sodium Carbonate

Trial	Vol. of acid calculated (ml.)	Vol. of acid used (ml.)	Difference in volumes (ml.)	Millim. of CO ₂ corresponding to this difference
0.8274 millimoles of sodium carbonate present in the solution titrated.				
1 (1)	52.18	52.82	0.64	0.01289
2 (1)	43.47	43.98	0.51	0.01027
3 (1)	37.19	37.75	0.56	0.01128
0.8096 millimoles of sodium carbonate present in the solution titrated.				
1 (2)	34.87	35.73	0.86	0.01732
2 (2)	35.62	36.43	0.81	0.01632
3 (2)	36.89	37.89	1.00	0.02015
4 (2)	34.42	35.40	0.98	0.01974
0.4045 millimoles of sodium carbonate present in the solution titrated.				
1 (1)	36.46	36.96	0.50	0.01007
2 (1)	38.58	39.16	0.58	0.01168
3 (2)	35.56	36.62	1.06	0.02135
4 (2)	35.11	35.99	0.88	0.01773

(1) Acid added slowly with vigorous agitation.

(2) Acid added slowly with mild agitation.

reacts during the titration. In an actual analysis, more acid would be used than theoretically called for indicating that less base had been consumed than should be. This would lead to low results for carbon dioxide. It was noticed that the end point was less distinct than when the base was titrated alone. Table 8 indicates that better results

are obtained with vigorous shaking of the solution and that the error is about 0.01 millimoles of carbon dioxide and is independent of the amount of carbonate present.

The analysis of measured samples of carbon dioxide was undertaken. A nitrometer bulb was fitted with a rubber stopper at the base that fitted the 500 ml. titration flask. The cup on top of the nitrometer bulb was fitted with another rubber stopper which held a drying tube filled with Ascarite and had a larger hole bored in it that would accommodate the buret tip. A cork was placed in this hole to prevent air from entering the cup. The nitrometer tube was evacuated by means of the vacuum pump and attached to the gas buret by means of nitrometer tubing. A cylinder of commercial grade carbon dioxide was connected to the side arm of the T-tube. All connections were held by hose clamps. Fifteen milliliter samples of carbon dioxide were added to the nitrometer bulb in the same manner as that in which the methyl chloride was added to the explosion flask. The cup at the top of the bulb was rinsed out with carbon dioxide free air and about 45 ml. of the barium hydroxide-barium chloride solution added to the nitrometer bulb through the cup directly from the buret. During this operation and the operations of washing a little of the liquid was retained in the cup to prevent air from entering the bulb. The cup was then rinsed several times with carbonate free distilled water and the washings added to the nitrometer bulb. Finally the cork was placed in the stopper and the last of the water and air admitted to the bulb. In so doing, the air was first passed over the Ascarite to remove any carbon dioxide. This solution was shaken well and allowed to be in contact with the gases in the bulb for about forty minutes. The

nitrometer bulb was then placed on top of the 500 ml. flask previously rinsed out with alcohol vapors and the solution drained into the flask. The sides of the bulb were carefully washed with carbonate free distilled water by placing the entire apparatus under the carboy containing the water and adding the water directly to the nitrometer bulb through the cup. The water ran down the sides of the bulb directly into the titration flask. Washing was continued until the volume of the solution reached 150 ml. The nitrometer bulb was removed from the titration flask, the latter was quickly stoppered, and titrated with acid as before.

Before being used again, the nitrometer bulb was cleaned with concentrated hydrochloric acid, cleaning solution, rinsed well with distilled water and dried.

The volume of the acid used in the back titration was subtracted from the volume of the acid calculated to be necessary to neutralize the base added and the difference in volumes multiplied by a factor that gave the millimoles of carbon dioxide in the sample. The ideal gas equation was used to calculate the size of the sample because the titration of the base in the presence of sodium carbonate indicated an error that would be larger than any error introduced in the calculation. The results of eight analyses are given in Table 9.

Trial 3 shows an unusually large deviation from the others. Since the analysis is subject to errors introduced in measuring out the gas sample, this result may be disregarded with some degree of safety. On this basis the mean error is 0.0091 millimoles or 1.52 per cent which agrees fairly well with what was predicted from the titration of the base with sodium carbonate added.

In order to determine if the concentration of the base had

Table 9

Results of Analyses of Measured Quantities
of Carbon Dioxide

Trial	Millim. of CO ₂ taken	Millim. of CO ₂ found	Error (Millim.)	Percentage error
1	0.5845	0.5798	- 0.0047	- 0.80
2	0.6750	0.6656	- 0.0094	- 1.39
3	0.5755	0.5762	+ 0.0007	+ 0.12
4	0.5601	0.5488	- 0.0113	- 2.02
5	0.5886	0.5764	- 0.0122	- 2.07
6	0.5960	0.5852	- 0.0108	- 1.81
7	0.6133	0.6086	- 0.0047	- 0.77
8	0.6056	0.5949	- 0.0107	- 1.77

changed by some accident during the investigation, samples were titrated with the acid as before. On the basis of three titrations the mean normality was found to be 0.05044. The normality from the original standardization was 0.05043 which indicates no change.

ANALYSIS OF SYNTHETIC MIXTURES OF METHYL CHLORIDE
AND CARBON DIOXIDE

Mixtures of known composition were prepared by measuring samples of methyl chloride and carbon dioxide with the gas buret and adding them to previously evacuated gas storage bulbs. The ratio of the quantities of gases was approximately the same as would be encountered in the products of pyrolysis of methyl chlorocarbonate. The methyl chloride was determined by the combustion method as described previously using 0.0082 N potassium thiocyanate and approximately 0.013 N silver nitrate solutions. The thiocyanate was standardized against silver nitrate and on the basis of three different weighings with four titrations for each weighing the average deviation from the mean was 1.37 parts per thousand. Thirty milliliters of the mixture was taken for the carbon dioxide determination which was made in the manner previously described. Tables 10 and 11 show the results of two combustions and two carbon dioxide determinations made on each sample. The ideal gas equation was used to calculate the composition of the gas mixtures and the size of the samples taken for analysis.

The precision in the determination of the chloride in the titration of the products of combustion was much poorer than expected. Table 12 gives the deviation from the mean for the various combustions in parts per thousand. The amount of precipitate in the titration of the products of combustion was quite small compared to the amount

Table 10

Analysis of Gas Mixture 1

Composition of the mixture by synthesis:

Methyl chloride	47.72 %
Carbon dioxide	52.28 %

Percentage methyl chloride from combustions:

Combustion 1	47.79 %
Combustion 2	46.32 %
Mean	47.06 %
Error	0.66 % Low

Percentage carbon dioxide:

Sample 1	51.61 %
Sample 2	51.15 %
Mean	51.38 %
Error	0.90 % Low

Table 11

Analysis of Gas Mixture 2

Composition of the mixture by synthesis

Methyl chloride	52.34 %
Carbon dioxide	47.66 %

Percentage methyl chloride from combustions:

Combustion 1	52.15 %
Combustion 2	52.26 %
Mean	52.21 %
Error	0.13 % Low

Percentage carbon dioxide:

Sample 1	46.51 %
Sample 2	44.84 %
Mean	45.68 %
Error	11.98 % Low

formed in the titration of blank which made the color comparison quite difficult. Better results were obtained when a little barium sulfate was added to the determination as was done with the analysis of Mixture 2.

Table 12

Average Deviation from the Mean for the Chloride Determination
in the Analysis of Synthetic Gas Mixtures

Combustion	Number of titrations	Average Deviation from the mean (parts per thousand)
Mixture 1		
1	2	5.06
2	3	16.60
Mixture 2		
1	3	4.74
2	3	7.46

SUMMARY AND CONCLUSIONS

The analysis of commercial methyl chloride by exploding a sample of the gas with the stoichiometric ratio of oxygen, the absorption of the products in sodium hydroxide and the titration of the chloride ion in the latter with silver nitrate solution using dichlorofluorescein indicator gives a mean error of 3.29 per cent low and a standard deviation of 1.41 per cent on the basis of forty-one trials. The error was found to be independent of the size of the sample taken, the ratio of the volume of oxygen to that of methyl chloride, the pressure in the flask at the time of explosion, the time of contact of the absorbent with the products of the combustion and the temperature of the gases at the time of explosion, within the limits investigated. This error cannot be explained by impurities in the sample as a combustion analysis of the methyl chloride used gave an error of 0.40 per cent high. The explosion method may find some application in the estimation of the quantity of methyl chloride but is certainly not quantitative.

The modified Winkler determination of carbon dioxide based on absorbing the gas in barium hydroxide solution and titrating the excess base to a faint pink with standard hydrochloric acid in the presence of excess barium ion using phenolphthalein as the indicator shows an almost constant loss of 0.01 millimoles of carbon dioxide. This error seems to depend upon the manner in which the titration

was carried out and independent of the amount of barium carbonate present. This error was attributed to some of the precipitated carbonate reacting with the hydrochloric acid.

When mixtures of methyl chloride and carbon dioxide were analyzed for methyl chloride by the combustion method and for carbon dioxide by the modified Winkler method, the mean error for the methyl chloride was 0.40 per cent low and for the carbon dioxide was 1.50 per cent low. The analysis for methyl chloride appears satisfactory but the analysis for carbon dioxide leaves much to be desired.

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