

THE USE OF INFRARED SPECTROPHOTOMETRY FOR THE ESTIMATION OF SMALL QUANTITIES OF SOME HALOGENATED HYDROCARBONS¹

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ABSTRACT

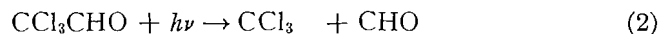
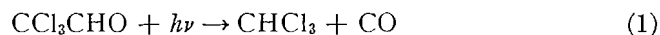
The infrared spectra of chloral, carbon tetrachloride, and chloroform have been determined between 1500 and 650 cm^{-1} over a range of pressures in the gas phase. Absorption bands suitable for the quantitative analysis of binary and ternary mixtures of the components have been selected and their peak intensities shown to obey Beer's Law over the range of pressures studied. Ternary mixtures have been analyzed from the spectra with an accuracy of about 20%.

The spectra of dichloromethane and methyl chloride have also been measured under comparable conditions.

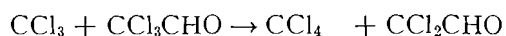
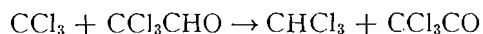
INTRODUCTION

Kinetic studies of the decomposition of many organic compounds have been made possible by the perfection of techniques used in estimating the small quantities of hydrocarbons that are produced when the decomposition is studied at low conversions. Investigations of the degradation of chlorine-containing compounds have been somewhat handicapped by the difficulties encountered in the analysis of halogenated hydrocarbons in a large excess of the parent substance.

The present problem arose in connection with the photolysis of chloral. This reaction, if analogous to that of acetaldehyde, proceeds by: (1) an intermolecular rearrangement and/or (2) rupture of the C-C bond:



followed by the abstraction reactions



Carbon monoxide was found to be the only 'noncondensable' product in a preliminary photolysis of chloral, but presumably because of insufficient differences in the vapor pressures of the condensable products, no other pure components could be isolated by distillation from a Ward still. It seemed reasonable to assume that the mixture resulting from the photolysis of chloral contained chloroform and carbon tetrachloride in a large excess of the aldehyde.

This paper describes a method of detecting and estimating the components of a mixture of chloral, carbon tetrachloride, and chloroform with the infrared spectrophotometer.

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EXPERIMENTAL

Apparatus

The optical cell was of pyrex, 10 cm. long, to which plane polished sodium chloride windows were affixed with Benolite cement. The cylindrical cell, of total volume 139.3 cc., was provided with a stopcock and ground glass joint to permit filling and evacuation, and a cold finger for condensation of gas samples.

The gas samples to be analyzed were prepared in a suitable high vacuum line containing liquid air traps, calibrated volumes, and a high speed, two-stage mercury diffusion pump. Dow Corning high vacuum silicone grease was used on all joints and stopcocks to minimize absorption of the samples. The optical densities of the gases were measured with a Perkin-Elmer Model 21 double beam recording infrared spectrophotometer (1, 4, 5) using a sodium chloride prism.

Materials

Chloral was a Fisher Scientific Company product of unspecified purity. It was distilled in air at a 5:1 reflux ratio. The portion boiling constantly at 97.8° C. was distilled *in vacuo* through a U-tube containing anhydrous phosphorus pentoxide and stored in a dark brown bottle. This product had a vapor pressure of 49.5 mm. at 24.4° C. and melted at -59° C.

Carbon tetrachloride, reagent grade, was obtained from Merck and dichloromethane, research grade, from Anachemia. Both compounds were distilled *in vacuo* and stored in the dark.

Chloroform was a Mallinckrodt analytical reagent grade product. It was passed through a column of silica gel before use to remove traces of alcohol and water.

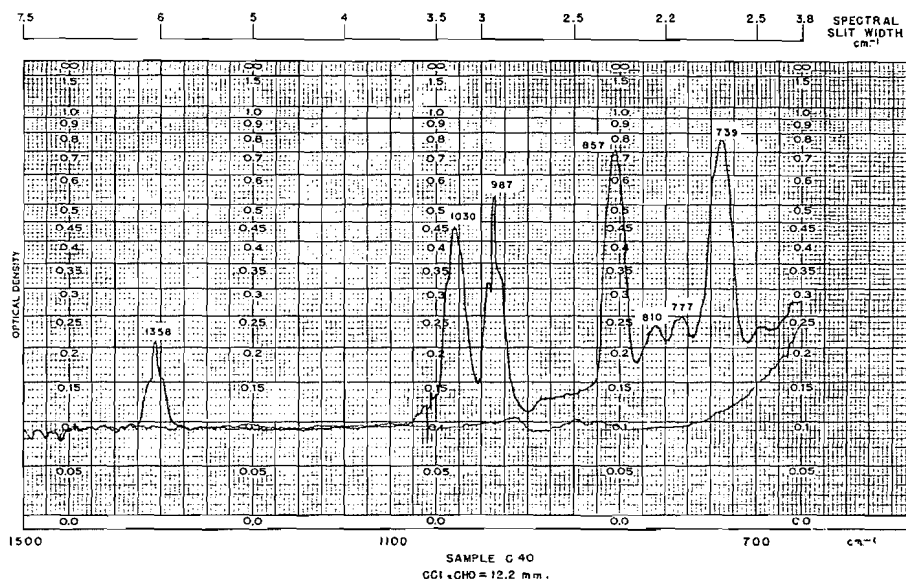


FIG. 1. Infrared spectrum of chloral (12.2 mm.).

Methyl chloride of unspecified purity was obtained from the Matheson Company and was purified by repeated bulb-to-bulb distillations *in vacuo*.

RESULTS AND DISCUSSION

Spectra of the Individual Components

Typical infrared spectra of chloral, carbon tetrachloride, and chloroform

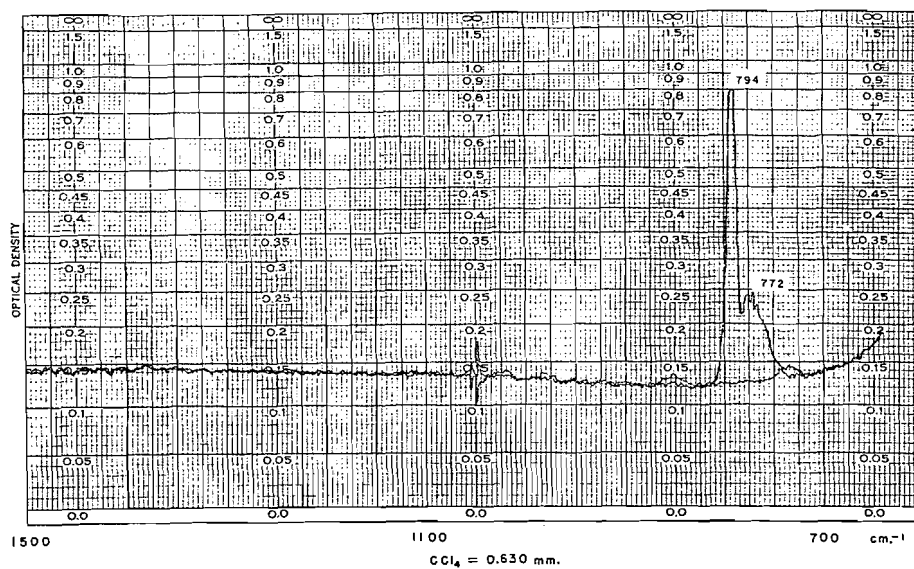


FIG. 2. Infrared spectrum of carbon tetrachloride (0.630 mm.).

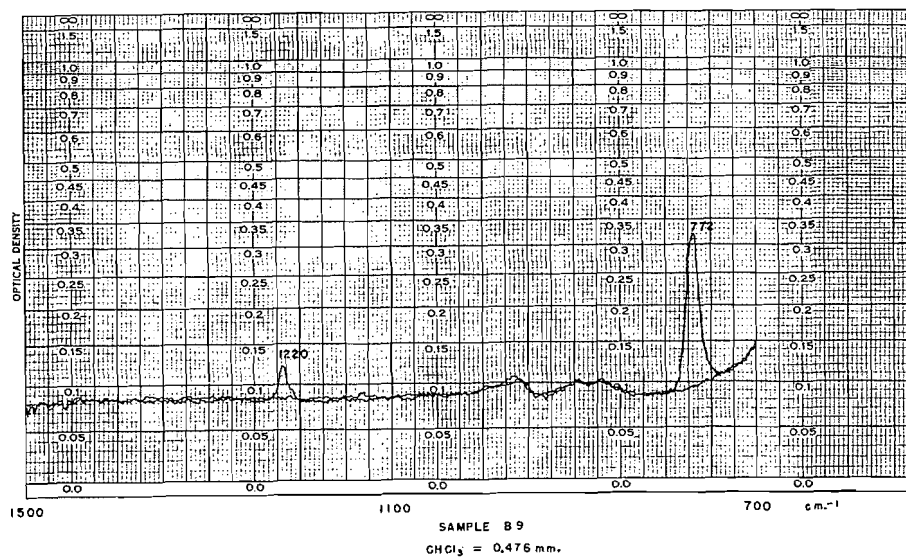


FIG. 3. Infrared spectrum of chloroform (0.476 mm.).

are reproduced in Figs. 1-3 respectively. All measurements were made at comparable spectral slit widths without a matching optical cell in the control beam of the spectrophotometer. The lower lines in Figs. 1-3 were obtained with the optical cell evacuated and all optical densities were measured from these reference lines. Inspection of these spectra suggested that the strong band of carbon tetrachloride at 794 cm^{-1} and the weaker, but distinctive band of chloroform at 1220 cm^{-1} might serve most conveniently for the analysis of these two components. The stronger chloroform band at 772 cm^{-1} is less suitable because of overlap with both carbon tetrachloride and chloral absorp-

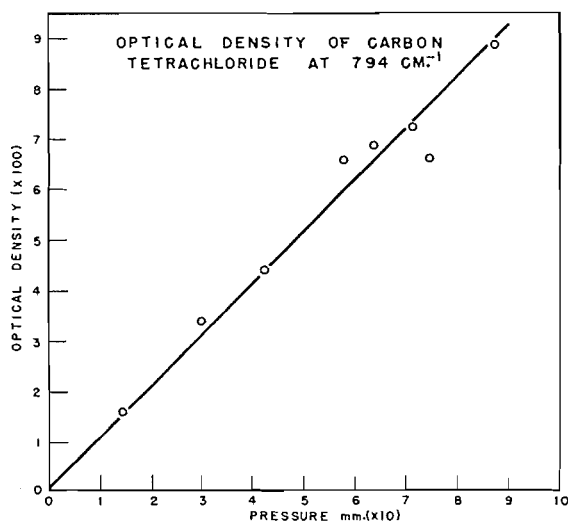


FIG. 4. Optical density of carbon tetrachloride at 794 cm^{-1} .

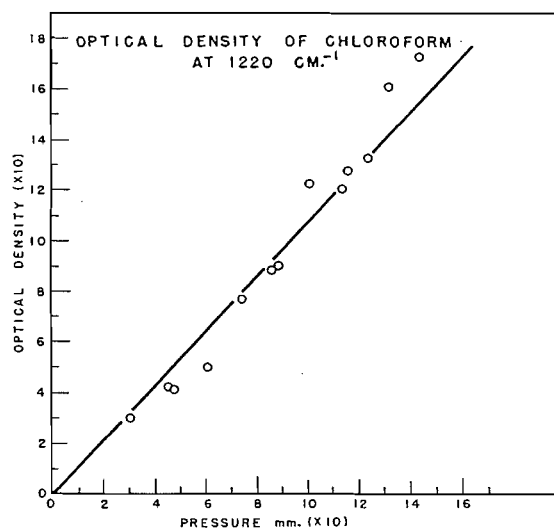


FIG. 5. Optical density of chloroform at 1220 cm^{-1} as a function of pressure.

tion. The conformity of these bands with Beer's Law is shown by the linear plots of peak optical density against partial pressure in Figs. 4 and 5. The numerical data are given in Tables I and II.

TABLE I
OPTICAL DENSITY OF CARBON TETRACHLORIDE

Sample	Pressure, mm.	Optical density	
		794 cm^{-1}	772 cm^{-1}
A8	0.421	0.440	0.076
A9	0.292	0.338	0.056
A10	0.120	0.156	0.026
A11	0.633	0.686	0.120
A12	0.742	0.685	0.133
A13	0.710	0.720	0.133
A14	0.869	0.885	0.180
A16	0.568	0.656	0.116

TABLE II
OPTICAL DENSITY OF CHLOROFORM

Sample	Pressure, mm.	Optical density	
		769 cm^{-1}	1220 cm^{-1}
B1	0.574	0.266
B2	1.41	0.695
B3	1.16	0.660	0.127
B4	0.859	0.450	0.088
B5	1.32	0.726	0.160
B6	1.44	0.800	0.172
B7	0.888	0.467	0.090
B8	1.01	0.601	0.122
B9	0.476	0.225	0.041
B10	0.746	0.392	0.077
B11	1.14	0.582	0.120
B12	0.457	0.213	0.042
B13	1.24	0.610	0.132
B14	0.304	0.142	0.030
B15	0.610	0.285	0.050

Chloral in the liquid phase exists in equilibrium with its trimer. The latter can be removed by simple distillation, but the equilibrium concentration of the trimer, about 10% (3), is attained on standing. The presence of the trimer in the gas phase, however, was not detected: there were no significant differences between the infrared spectrum of stored chloral and that of the freshly distilled material. The aldehyde absorbs moisture to precipitate the hydrate and decomposes readily on exposure to light or oxygen in the atmosphere (2). To obtain reproducible spectra it was necessary to dry the chloral quite frequently by passage over phosphorus pentoxide and to store it in the dark after distillation.

The infrared spectrum of chloral has major peaks at 1358, 1030, 987, 857, and 739 cm^{-1} , and two small maxima at 777 and 810 cm^{-1} . The relative magnitudes of absorption at 857, 739, 777, and 810 cm^{-1} were useful criteria for

purity of the aldehyde. Pure chloral is practically transparent at 1250–1200 cm^{-1} . The appearance of appreciable structure in this region probably denotes decomposition of the compound. This phenomenon is of importance because of overlap with the peak at 1220 cm^{-1} in the spectrum of chloroform. The optical densities of chloral at 794 cm^{-1} and 772 cm^{-1} were also measured because the spectrum of carbon tetrachloride shows maxima at these positions and there are no peaks in the carbon tetrachloride spectrum where chloral is transparent. The data for the optical densities of chloral at the important

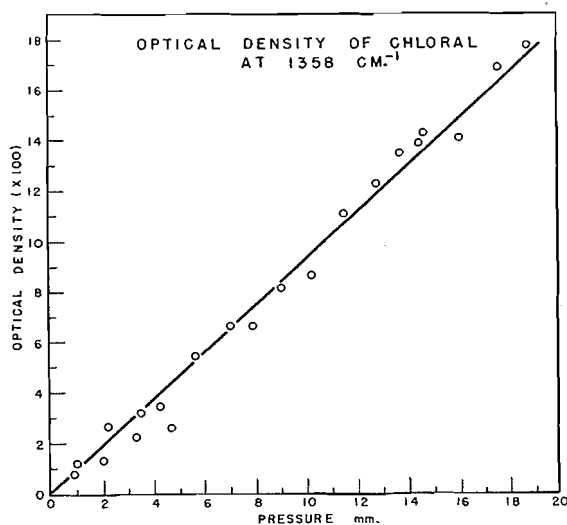


FIG. 6. Optical density of chloral at 1358 cm^{-1} as a function of pressure.

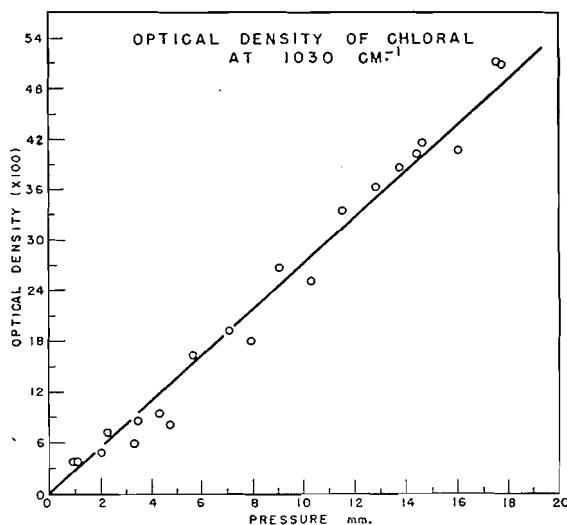


FIG. 7. Optical density of chloral at 1030 cm^{-1} as a function of pressure.

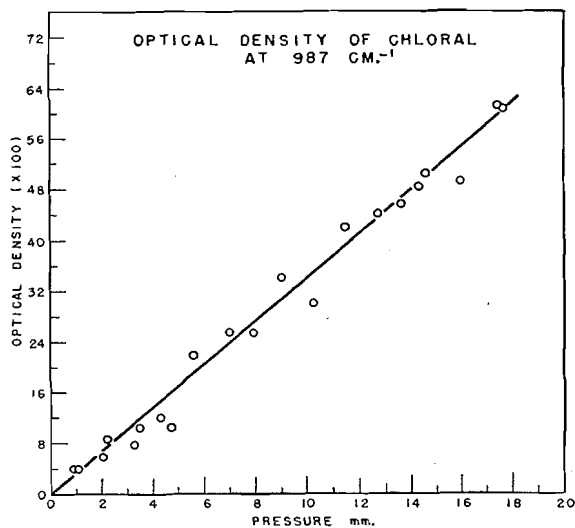


FIG. 8. Optical density of chloral at 987 cm.^{-1} as a function of pressure.

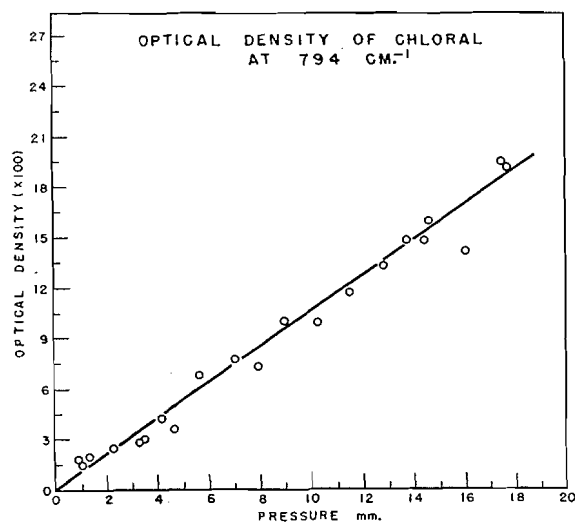


FIG. 9. Optical density of chloral at 794 cm.^{-1} as a function of pressure.

wave numbers are collected in Table III, and the conformity with Beer's Law established by the linear plots in Figs. 6-9.

Spectra of Mixtures

Table IV lists the analytical results obtained for a series of mixtures of chloral, carbon tetrachloride, and chloroform. The infrared spectrum of a typical mixture is reproduced in Fig. 10.

Chloroform and carbon tetrachloride are transparent at 1358 , 1030 , 987 , and 857 cm.^{-1} where chloral has spectral peaks. The optical densities at these

TABLE III
OPTICAL DENSITY OF CHLORAL

Sample	Pressure, mm.	Optical density, cm. ⁻¹						
		1358	1030	987	857	794	772	739
1C	10.24	0.086	0.251	0.300	0.523	0.097	0.106	0.512
3C	13.70	0.134	0.383	0.455	0.650	0.147	0.153	0.652
4C	14.60	0.142	0.412	0.505	0.714	0.158	0.160	0.713
5C	17.50	0.168	0.508	0.610	0.816	0.194	0.212	0.810
13C	5.59	0.054	0.162	0.216	0.342	0.067	0.094	0.338
14C	7.91	0.066	0.176	0.252	0.382	0.073	0.105	0.386
15C	4.68	0.026	0.080	0.104	0.162	0.035	0.047	0.162
16C	3.47	0.032	0.083	0.104	0.166	0.030	0.036	0.166
17C	3.29	0.022	0.060	0.078	0.126	0.028	0.035	0.133
18C	2.00	0.013	0.048	0.058	0.085	0.020	0.023	0.096
19C	0.911	0.008	0.038	0.043	0.061	0.018	0.022	0.070
30C	7.00	0.066	0.192	0.254	0.364	0.076	0.074	0.394
31C	16.00	0.140	0.404	0.490	0.718	0.140	0.143	0.702
32C	14.40	0.138	0.398	0.482	0.712	0.146	0.140	0.702
33C	11.45	0.110	0.332	0.418	0.614	0.116	0.116	0.623
34C	12.80	0.122	0.360	0.440	0.676	0.132	0.128	0.668
35C	17.70	0.170	0.508	0.605	0.858	0.190	0.198	0.860
36C	1.02	0.012	0.036	0.043	0.060	0.015	0.014	0.074
37C	9.00	0.081	0.266	0.340	0.510	0.099	0.094	0.522
38C	4.28	0.034	0.094	0.120	0.194	0.039	0.035	0.196
39C	2.20	0.026	0.074	0.087	0.143	0.025	0.025	0.145

TABLE IV
ANALYSIS OF SYNTHETIC MIXTURES

Sample	Composition of mixture, mm.	Infrared analysis,* mm.
M1	CCl ₃ CHO: 8.52 CCl ₄ : 0.312	CCl ₃ CHO: 9.9 CCl ₄ : 0.27
M2	CCl ₃ CHO: 18.9 CCl ₄ : 0.328	CCl ₃ CHO: 19.9 CCl ₄ : 0.30
M3	CCl ₃ CHO: 10.1 CHCl ₃ : 0.610	CCl ₃ CHO: 10.8 CHCl ₃ : 0.55
M4	CCl ₃ CHO: 4.61 CHCl ₃ : 0.821	CCl ₃ CHO: 4.3 CHCl ₃ : 0.65
M6	CHCl ₃ : 0.719 CCl ₄ : 0.802	CHCl ₃ : 0.78 CCl ₄ : 0.70
M7	CHCl ₃ : 0.558 CCl ₄ : 0.630	CHCl ₃ : 0.50 CCl ₄ : 0.44
M8	CCl ₃ CHO: 5.56 CCl ₄ : 0.480 CHCl ₃ : 0.462	CCl ₃ CHO: 5.0 CCl ₄ : 0.57 CHCl ₃ : 0.49
M9	CCl ₃ CHO: 5.13 CCl ₄ : 0.470 CHCl ₃ : 0.330	CCl ₃ CHO: 4.8 CCl ₄ : 0.40 CHCl ₃ : 0.31

* The data for chloral in this column are average values from optical density measurements at appropriate wave numbers.

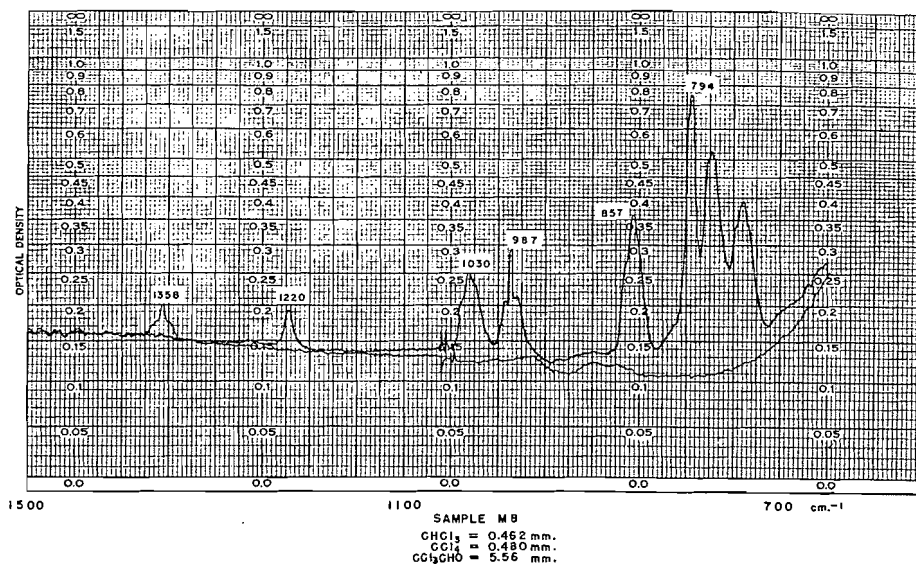


FIG. 10. Infrared spectrum of a typical mixture of chloroform, carbon tetrachloride, and chloral.

wave numbers, obtained from the infrared spectrum of a mixture of chloral, carbon tetrachloride, and chloroform, then give directly the concentration of chloral in the mixture. The chloroform content is measured similarly from the optical density at 1220 cm^{-1} since the spectra of both carbon tetrachloride and chloral show no structure at this wave number.

Since chloroform is practically transparent at 794 cm^{-1} , the optical density of the mixture at this wave number, less the contribution of the previously determined quantity of chloral, is used to estimate the concentration of carbon tetrachloride.

A sample calculation is given for the analysis of sample M8:

Optical density at 1358 cm^{-1}	= 0.054,	equivalent to 5.5 mm. chloral
“ “ “ 1030 cm^{-1}	= 0.128,	“ “ 4.7 mm. “
“ “ “ 987 cm^{-1}	= 0.166,	“ “ 5.0 mm. “
“ “ “ 857 cm^{-1}	= 0.247,	“ “ 4.9 mm. “

Mean value of concentration of chloral = 5.0 mm.

Optical density at 1220 cm^{-1} = 0.054, equivalent to 0.49 mm. chloroform

Optical density at 794 cm^{-1} = 0.650

Optical density at 794 cm^{-1} due to 5.0 mm. of chloral = 0.054

“ “ “ “ “ “ 0.49 mm. “ chloroform = 0.000

“ “ “ “ “ “ carbon tetrachloride

= $0.650 - 0.054$

= 0.596, equivalent to 0.57 mm. of carbon tetrachloride.

The deviations between the data for the synthetic mixtures and those obtained spectrophotometrically in Table IV are due mainly to the difficulty

in preparing mixtures whose composition in the gas phase is accurately known. The chlorinated compounds dissolve to some extent in the Silicone grease used in the vacuum line and the Benolite cementing the sodium chloride windows to the pyrex optical cell. The extent of absorption is a function of the time of exposure of the compounds to grease, the surface area of the grease, and the pressure at which the gaseous sample is prepared. Under these circumstances, it is not feasible to make empirical corrections for the absorption effects.

A standard procedure in preparing and analyzing the samples was adhered to as closely as possible. While reproducible data were obtained in this way, it is felt that the elimination of stopcocks wherever possible would considerably increase the accuracy of analysis of these chlorinated compounds by infrared spectrophotometry.

Spectra of Other Chlorinated Hydrocarbons

With a view to extending these studies to more complex mixtures of chlorinated hydrocarbons, the infrared spectra of dichloromethane and methyl chloride have also been measured at 1 mm. and 10 mm. respectively under comparable experimental conditions.

The absorption bands in these compounds are relatively weak; dichloromethane showed maxima at 1277, 1262, 762, and 747 cm^{-1} and methyl chloride at 1370, 1340, 745, 726, and 710 cm^{-1} .

ACKNOWLEDGMENTS

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