



TEST METHOD

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DOWM 100106

Supersedes: (New)

Trace Impurities in Liquid Chlorine by Infrared Spectroscopy

1. Scope

This method is applicable to the determination of methyl chloride, methylene chloride, chloroform, carbon tetrachloride, carbon dioxide, and water in liquid chlorine. The method is useful over the following concentration ranges:

<u>Component</u>	<u>Concentration Range (pg/g)</u>
Methyl chloride	7-115
Methylene chloride	5-26
Chloroform	3-45
Carbon tetrachloride	2.3-28
Carbon dioxide	2.5-19
Water	0.5-25

The method has not been validated for the determination of phosgene, dichlorodifluoro methane and other chlorinated organics, but indications are that it may be useful for analysis for these components.

2. Principle

A liquid chlorine sample is introduced into a special infrared cell. The desired portion of the infrared spectrum is scanned and concentrations of selected impurities are determined from previously prepared calibration curves and response factors.

3. Safety

- 3.1 Each analyst should be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information for products should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.
- 3.2 Chlorine is a corrosive and toxic material. Chlorine should be stored and handled in a hood approved for chlorine use. Chlorine should be sampled only with adequate eye protection, gloves, and an appropriate respirator. Emergency procedures in the event of the release of the contents of a cylinder should be developed and thoroughly communicated to all workers in the immediate area. Contact with liquid or gaseous chlorine can cause severe burns and severe respiratory injury.
- 3.3 Overfilling of the sample container and/or cell can result in component failure and subsequent release of chlorine. Precautions and procedures designed to prevent overfilling should be employed.

4. Apparatus

- 4.1 Infrared spectrophotometer, such as the Perkin-Elmer Model 598, available from Perkin-Elmer Corp., Norwalk, CT.
- 4.2 Infrared cell, custom constructed as shown in Figure 1.
- 4.3 Silver chloride windows, 0.5 mm x 2.5 mm, available from Harshaw Chemical Company, 6801 Cochran Road, Solon, OH 44139.
- 4.4 Tantalum stock, suitable for machining, available from Ref Welding and Fabrication, P. O. Box 40511, 4128 Creekmont, Houston, TX.
- 4.5 Kelrez sheet, for infrared cell, 0.030 inch thickness, available from E. I. duPont de Nemours Co., Wilmington, DE 19898.

5. Reagents

- 5.1 Methyl chloride, technical grade, available from The Dow Chemical Company, Texas Operations, Freeport, TX 77541.
- 5.2 Methylene chloride, distilled in glass, available from MCB.
- 5.3 Chloroform, distilled in glass, available from MCB.
- 5.4 Carbon tetrachloride, distilled in glass, available from MCB.
- 5.5 Perchloroethylene, technical grade, available from The Dow Chemical Company, A-2429, Texas Operations, Freeport, TX 77541.
- 5.6 1,1,1-Trichloroethylene, technical grade, available from The Dow Chemical Company, Texas Operations, Freeport, TX 77541.
- 5.7 Hexachloroethane, available from Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI.
- 5.8 Carbon dioxide, available from Matheson Gas.
- 5.9 Hydrochloric acid, reagent grade, available from most chemical supply companies.

6. Procedure

- 6.1 Sample Procedure
 - 6.1.1 Obtain a sample of liquid chlorine in a pre-weighed, 1-liter tantalum cylinder equipped with two nickel valves and a dip pipe (Figure 2). Weigh the cylinder which contains the liquid chlorine and record its weight. The cylinder should contain approximately 75% liquid chlorine with the rest being vapor.
 - 6.1.2 Attach the cylinder and the IR cell to the filling apparatus (Figure 3). Check to be sure that all valves are closed prior to filling the IR cell.
 - 6.1.3 Open valve A. Flush the filling apparatus by partially opening valve B for a few seconds and then close it.
 - 6.1.4 Fill the IR cell by opening valve C. Close valve C and flush the cell by opening valve D. Close valve D. &
 - 6.1.5 Repeat filling and flushing of the IR cell.

- 6.1.6 Fill the cell a final time. Close valves C and A.
 - 6.1.7 Vent chlorine from the filling apparatus by opening valve B.6.1.8 Remove the cell from the filling apparatus and check for adequate vapor space by inverting cell. Place the cell in the spectrophotometer and scan the infrared region. From the scan data, select the proper wavelengths and measure the corresponding absorbances.
 - 6.1.9 Calculate concentration³ for each analyte using response factors (See 7.0) and, if necessary, correct for liquid phase depletion, as may take place with CO₂ and methyl chloride. Liquid phase depletion curves for carbon dioxide and methyl chloride as a function of percent vapor phase are shown in Figures 4 and 5, respectively. Table I includes a list of primary and secondary wavelengths.
- 6.2 Calibration Procedures
- 6.2.1 Components other than water.
 - 6.2.1.1 Prepare calibration standards by adding known amounts of each impurity to a cylinder of liquid chlorine.
 - 6.2.1.2 Add the impurities, by means of a syringe, through a septum fitted to the cylinder.
 - 6.2.1.3 Construct calibration curves for each impurity.
 - 6.2.2 Water
 - 6.2.2.1 Compare water content of liquid chlorine samples found by the infrared procedure to those found by electrolytic hygrometer. (See 11.1)
 - 6.2.2.2 Construct a calibration curve for water to demonstrate linearity.
 - 6.2.2.3 Calculate a response factor for water by infrared (ppm H₂O found by electrolytic hygrometer/absorbance unit by IR).

7. Reagent Solutions

- 7.1 Calculate the concentration of each trace impurity from the following equation:

$$C = A \times RF$$

where:

C = concentration of the impurity in ppm ($\mu\text{g/g}$)
A = absorbance at analytical wavelength
RF = response factor at analytical wavelength (ppm/abs. unit)

- 7.2 Calculate the volume % vapor phase in the sample as follows:

$$D = \frac{\left(V - \frac{S}{E} \right)}{V} \times 100$$

where:

D = % vapor phase
V = container volume (mL)
S = sample weight (g)
E = density of liquid chlorine (1.6 g/mL)

- 7.3 Calculate the correction for depletion of carbon dioxide and methyl chloride as follows:

$$C_1 = \frac{C_2}{R} \times 100$$

where:

C 1 = corrected concentration in ppm (pg/9)
C 2 = concentration in liquid phase in ppm ($\mu\text{g/g}$)
R = % remaining in liquid phase (from depletion curve)

8. Precision and Recovery

8.1 The data obtained by analyzing a liquid chlorine sample, ten times by this procedure, is summarized below. The data was obtained for only those trace impurities currently being monitored in liquid chlorine.

	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CO ₂	H ₂ O
Concentration (µg/g)	16.2	4.9	6.6	4.5	15.3	1.6
Relative Std. Deviation %	8.6	17	16	14	3.5	23.6
Rel. Precision at 95% Confidence level	17.2	34	32	28	7.0	47.2

8.2 The percent recovery for the trace impurities shown above are summarized as follows. These data were obtained by analyzing ten different chlorine samples to which were added known amounts of standard impurities. By constructing calibration curves, it was established that the listed concentration ranges are linear. (See 10.1)

Trace Impurity	Concentration Range (µg/g)	% Recovery (Mean)	% Recovery (Range)
CH ₃ Cl	7-115	103	79-139
CH ₂ Cl ₂	5-26	86.9	72-109
CHCl ₃	3-45	96.8	85-121
CCl ₄	2.3-28	87.7	70-109
CO ₂	2.5-19	107	83-150

9. Detection Limits

9.1 Detection limits are based on the ability to detect and measure the absorbance at the wavelengths used in the procedure.

Trace Impurity	Detection Limit (µg/g)	Wavelength (Micron)
CH ₃ Cl	<5.0	7.5
CH ₂ Cl ₂	<2.0	7.9
CHCl ₃	<2.0	8.2
CCl ₄	<2.0	12.7
CO ₂	<1.0	4.35
H ₂ O	<0.2	6.3

10. Notes

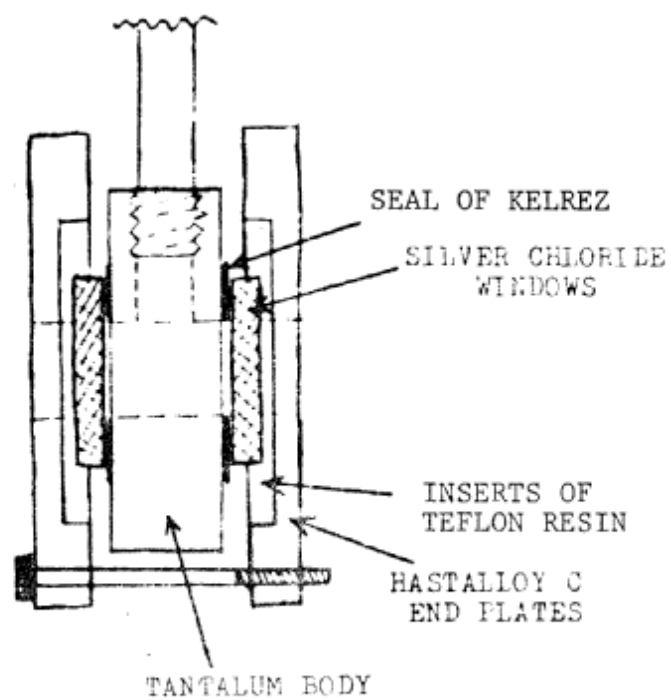
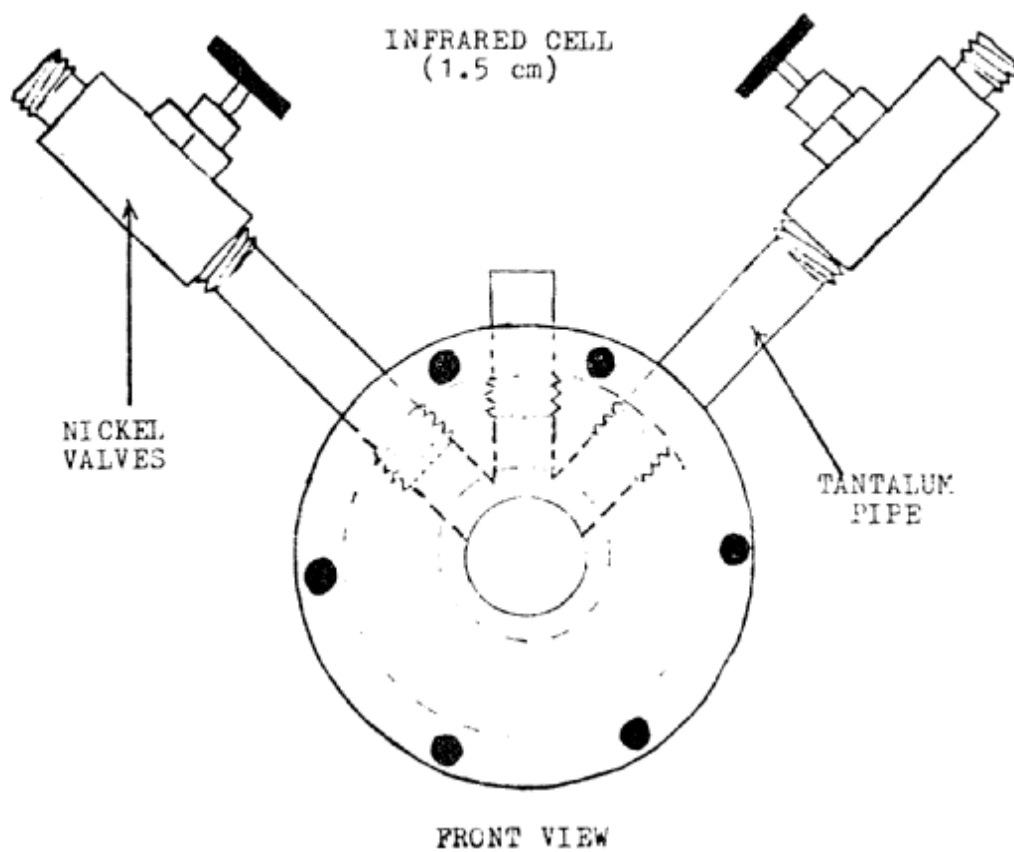
- 10.1 Calibration for water was done by direct comparison of infrared to on-line analysis by electrolytic analyzer at the 2 ppm level, therefore no range data is available.

11. References

- 11.1 International Standard ISO 2202-1972/Addendum 1, "Liquid Chlorine for Industrial Use - Determination of Water Content Using an Electrolytic Analyser", International Organization for Standardization, 1975.

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FIGURE 1



SIDE VIEW

FIGURE 2

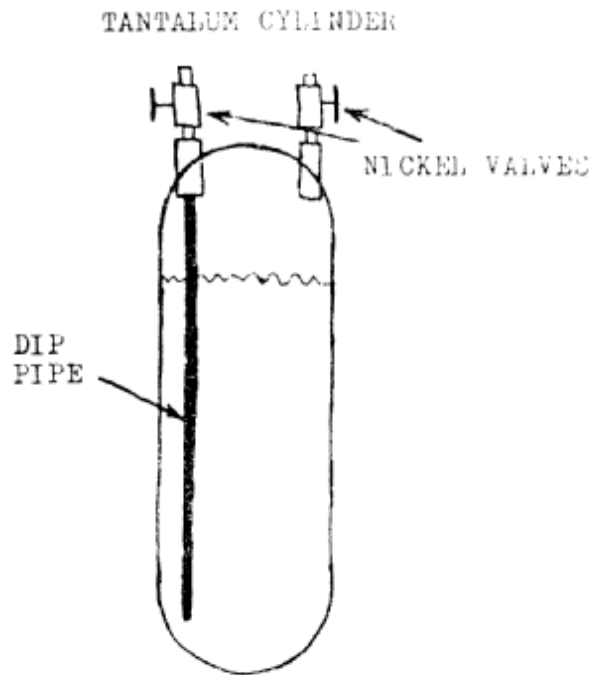


FIGURE 3

FILLING APPARATUS

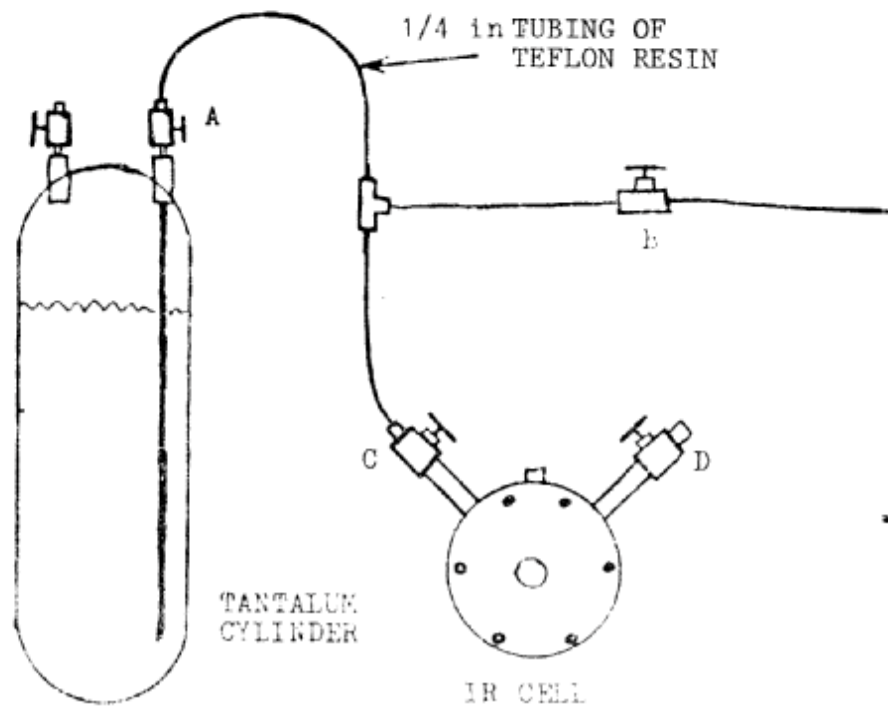


Figure 4
Depletion of Carbon Dioxide from Liquid Chlorine

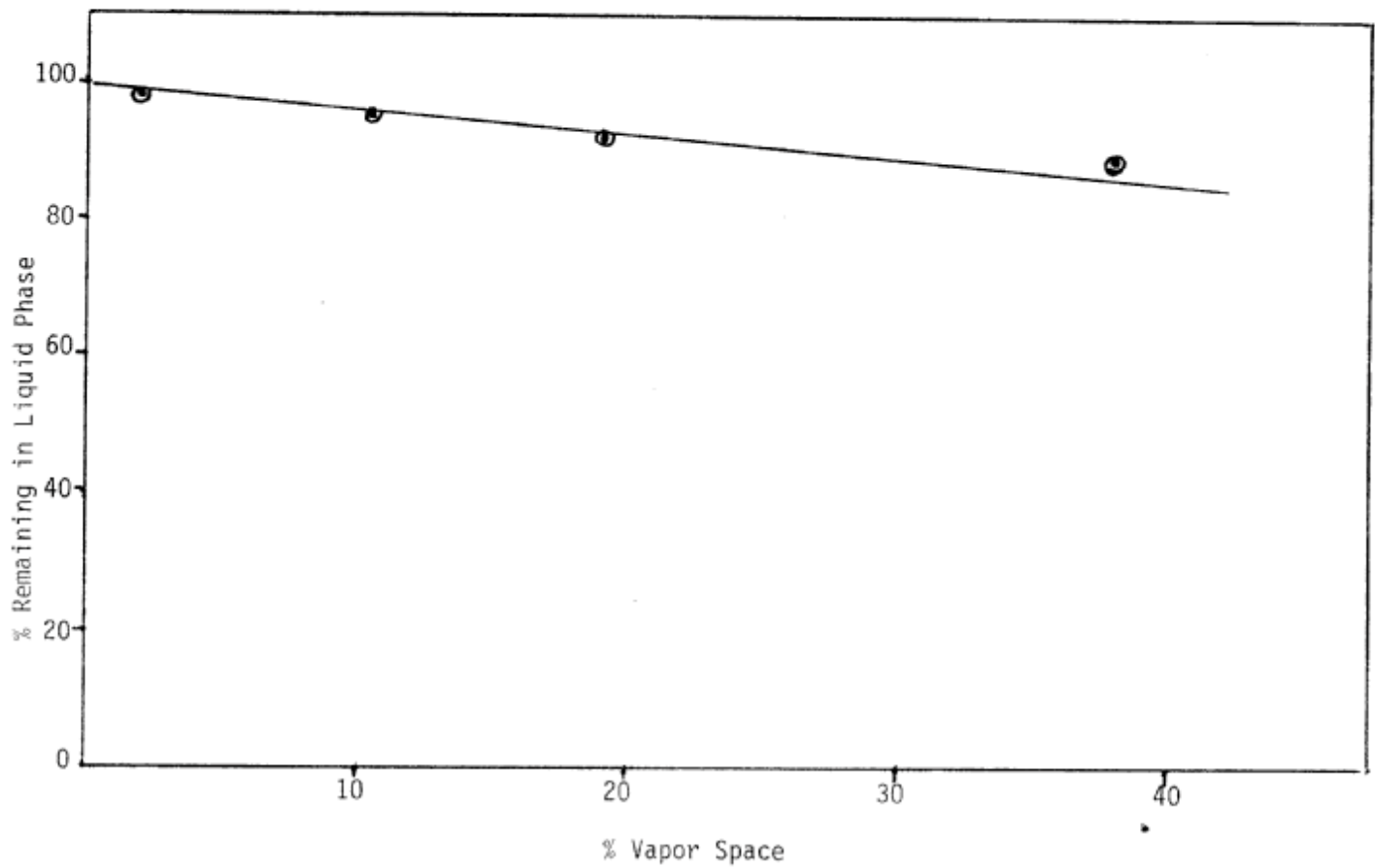


Figure 5
Depletion of Methyl Chloride from Liquid Chlorine

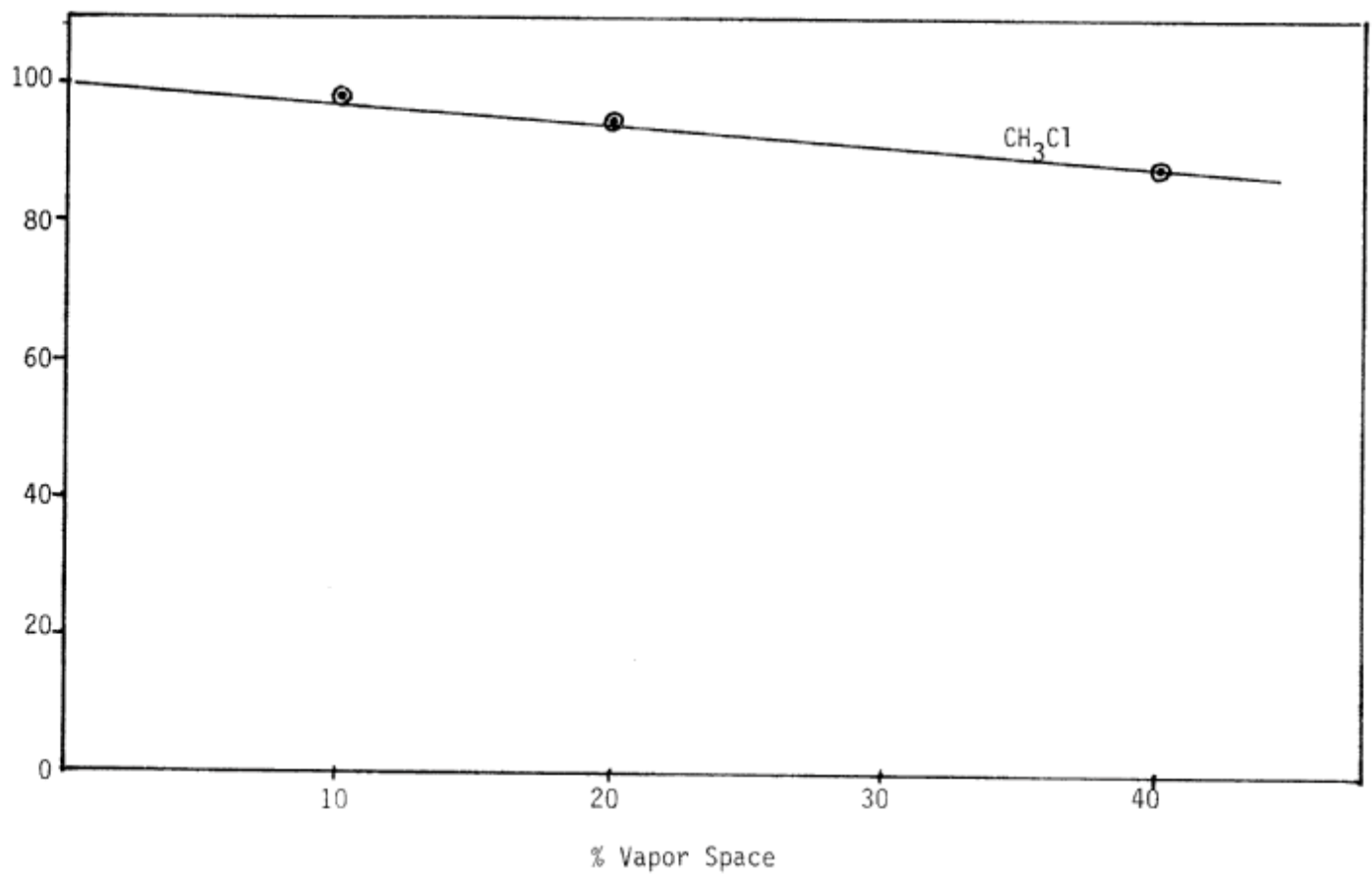


Table I.

Analytical Wavelengths

<u>TRACE IMPURITY</u>	<u>Calibrated Wavelength Microns</u>	<u>Additional Wavelengths⁽¹⁾ Microns</u>	<u>Interferences</u>
Methyl Chloride	3.42 7.5*	14.4	
Methylene Chloride	7.9* 13.5		
Chloroform	8.2* 13.2		CCl ₄ at 13.2 μ
Carbon Tetrachloride	12.7* 13.2		C ₂ Cl ₄ and C ₂ Cl ₆ at 12.7 μ CHCl ₃ at 13.2 μ
1,1,1 Trichloroethane	9.2* 13.9		Freon 12 at 9.2 μ
Perchloroethylene	11.0* 12.8		Freon 12 at 11.0 μ
Hexachloroethane	12.7	14.8	C ₂ Cl ₄ and CCl ₄ at 12.7 μ
Phosgene	11.9	5.58	
Freon 12	9.2 11.0*	8.8 11.4	C ₂ H ₃ Cl ₃ at 9.2 μ C ₂ Cl ₄ at 11.0 μ
Carbon Dioxide	4.35	2.72 2.80	H ₂ O at 2.72 μ and 2.80 μ
Water	6.3		
Hydrochloric Acid	3.58		

*Primary analytical wavelength -

(1) Additional absorbance bands observed but uncalibrated -