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## Measuring Chlorinated Hydrocarbons in Combustion by Use of Fourier Transform Infrared Spectroscopy

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■ The quantitative measurement of products of incineration of chlorinated hydrocarbons using Fourier transform infrared (FTIR) spectrometry was evaluated during a study of the fundamental processes of toxic waste incineration. Combustion products were sampled from a turbulent flow reactor into which chlorinated hydrocarbons were injected. Chlorinated species were detected mainly in the C-Cl stretching region, away from H<sub>2</sub>O and CO<sub>2</sub> interferences. Absorbances of species having rotational lines narrower than the instrument resolution, such as CO, CO<sub>2</sub>, and HCl, were nonlinear under most conditions. The measured absorbance of these species was very sensitive to total pressure, increasing with an increase in total pressure; at very low optical densities, however, absorbance became independent of total pressure. Thus, while FTIR spectroscopy has many features that make it attractive for measuring combustion species, care must be taken to ensure the accuracy of quantitative measurements.

### Introduction

Infrared absorption spectroscopy has long been used for molecular identification and quantification in a variety of chemical systems. Most molecules, with the exception of homonuclear diatomics such as N<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub>, absorb light

in the mid-infrared region (500-4000 cm<sup>-1</sup>). The development of Fourier transform infrared (FTIR) spectrometry in the 1970s greatly increased the speed, resolution, and sensitivity of measurements (1). Coupled to long path length cells, FTIR spectroscopy has provided a wealth of information about species at low concentrations, especially in the study of atmospheric phenomena (2-4). For many species the limit of detection is in the sub-ppm range (5).

FTIR spectroscopy has not been used extensively in combustion. One major problem is the presence of large quantities of water and carbon dioxide, molecules with numerous infrared absorption features. There have been some studies using FTIR spectroscopy for gas analysis (3, 6-11) and several for temperature measurements (8, 9, 12, 13). In addition, there has been research on the use of tunable diode laser spectroscopy for combustion products (14), and nondispersive infrared analyzers (NDIR) for single-species detection have been used extensively.

In studying the combustion of chlorinated hydrocarbons, we are using FTIR spectroscopy as our principal diagnostic technique. At the present time there are no simple methods for detecting chlorinated hydrocarbons during their incineration; several methods are currently being investigated (15, 16). Infrared analysis is attractive because the C-Cl stretching region is from 500 to 750 cm<sup>-1</sup> (17), a region relatively free from water and carbon dioxide interferences, and the spectra of HCl and other simple chlorine-containing species are well-known (18). The spectrometer has a large dynamic range, allowing quantification from the sub-ppm range to the percent range,

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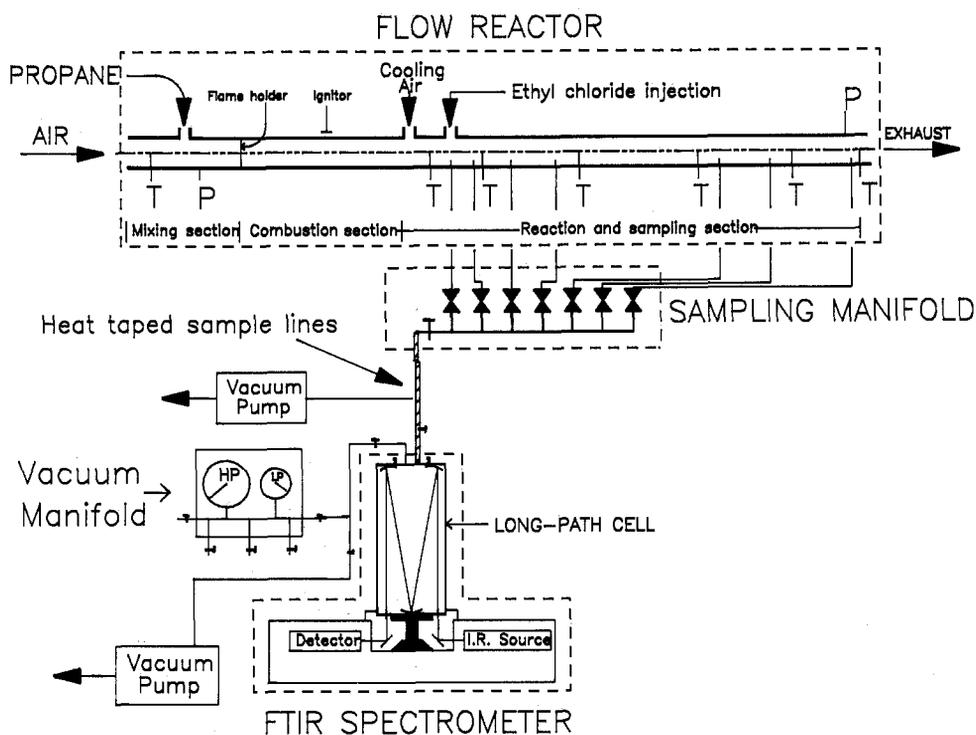


Figure 1. Schematic of experimental apparatus.

especially when used with adjustable path length cells. While not strictly a real-time method, measurement times are not excessive. A high-resolution interferogram ( $0.25\text{ cm}^{-1}$ ) of a sample may be taken in a few minutes, much faster than conventional GC analysis. The method also allows us to monitor most of the species present in normal hydrocarbon combustion using a single instrument. It is possible to adapt it for high-temperature in situ measurements (8, 9, 12, 13). Finally, the recent introduction (by several manufacturers) of relatively low cost, high-resolution FTIR spectrometers makes it an attractive choice for many laboratories.

The purpose of this paper is to report our findings on the use of an FTIR spectrometer to measure species produced by the reactions of chlorinated hydrocarbons. We have examined some of the difficulties encountered in the use and calibration of the spectrometer and in sampling of gases from a high-temperature flow reactor.

#### Experimental Apparatus

**Spectrometer.** The system consists of a long path cell coupled to a high-resolution ( $0.25\text{ cm}^{-1}$ ) FTIR spectrometer, Digilab Model FTS-40, with a cryogenically cooled MCT detector. The multipass cell employs White cell optics (19) and was manufactured by Infrared Analysis, Inc. The number of times the infrared beam traverses the cell can be readily changed from a minimum of 4 passes, producing a path length of 2.28 m, to a practical maximum of 40, with a path length of 22.8 m. All measurements presented here were made with a path length of 2.28 m. For most samples the total pressure in the cell was maintained at 100 Torr to prevent condensation of water from combustion, which avoids dissolving species present at low concentrations. In addition, condensed water with HCl is highly corrosive. Condensation in the cell can also be avoided by heating. We warmed the cell by wrapping it with heat tape but were unable to maintain good optical alignment, presumably due to mirror distortions. Heating the sample also changed the spectra by altering the populations of the energy states of the molecules. For these reasons the cell was unheated for all measurements.

**Flow Reactor and Sampling System.** A combustion-driven turbulent flow reactor is used to incinerate the chlorinated hydrocarbons. Propane-air mixtures are burned in the reactor, and chlorinated hydrocarbons are injected downstream of a flame holder. The experimental apparatus is shown in Figure 1. Samples are withdrawn from the reactor through  $3/16$  in. o.d. lines of 304 stainless steel; the desired sample location in the reactor is selected by opening the appropriate valve on the sample manifold. From the sample manifold the gas travels through a  $3/8$  in. o.d. flexible stainless steel line to the long path cell. The lines and manifold are warmed with heat tape to prevent condensation. A rotary vacuum pump is used to draw the sample through the line and the long path cell. Details regarding the design and operation of the flow reactor are found in ref 20.

Sampling begins after the flow reactor has reached a steady-state operating condition, indicated by stable temperatures; steady state is achieved in  $\sim 40$  min. Initially the sample cell is evacuated and products flow through the sample line only, bypassing the cell. This procedure brings the line to a steady-state point to minimize any adsorption and desorption effects. The next step is to draw the sample through the long path cell for approximately 5–10 min; the valves to the cell are then closed and the spectrum is scanned. While the sample is flowing through the cell the pressure is maintained at 100 Torr. A vacuum background spectrum is also recorded for sample normalization.

**Calibration Procedures.** To obtain a calibration spectrum for a particular species, a known amount of sample must be introduced into the cell. Gas-tight syringes of various sizes were used to introduce measured amounts of gas into the cell. The pure gas was drawn into the syringe by first flowing the gas from the cylinder through a line that emptied into a ventilation hood; the gas was then withdrawn from the line, into the syringe, through a septum mounted in a fitting in the line. A measured amount of gas was then injected into a stream of nitrogen, which flowed into the previously evacuated cell or was injected directly into the cell through a septum mounted on the cell. Nitrogen was added until the desired total

pressure was reached. To calculate the concentration within the cell, its volume was measured by using a Brooks flow meter standard consisting of a precision-bored glass cylinder with a mercury-sealed Teflon piston. The cell volume was found to be  $4.84 \text{ L} \pm 0.5\%$ . Repeatability and accuracy of the sample concentrations were found to be approximately  $\pm 1\%$  when the calibration spectra were recorded the same day as the sample spectra.

To calibrate liquids, approximately 0.5 mL of the liquid was placed in a glass finger. The finger was then attached to a valve on the calibration manifold and frozen by immersing the finger in liquid nitrogen. After the air was evacuated from the finger, the valve was closed and the sample warmed. The valve was reopened partially to allow vapor from the liquid to fill the evacuated cell-manifold system to a desired partial pressure. Nitrogen was added to fill the cell to 100 Torr and the spectrum measured. This technique was not as accurate as gas measurements made by the syringe method due to errors associated with the pressure measurements.

### Absorption Spectroscopy

**Qualitative Measurements.** Each molecular species that absorbs in the infrared has its own characteristic absorption spectrum, which allows us to determine its presence. Reference spectra for qualitative identification were obtained from samples of pure compounds or from published IR spectra (21). Identification can be difficult, however, for species having overlapping spectra. Hydrocarbons, for example, have a strong absorption band near  $3000 \text{ cm}^{-1}$  due to the C-H stretch. Consequently, other regions must be used for identification of most hydrocarbons. Interferences from water can be especially troublesome because water absorbs strongly from  $1300$  to  $1950 \text{ cm}^{-1}$  and from  $3500$  to  $3950 \text{ cm}^{-1}$ . Carbon dioxide has strong absorption features in the regions from  $630$  to  $720 \text{ cm}^{-1}$  and from  $2250$  to  $2390 \text{ cm}^{-1}$ . We have found, however, that the absorption bands in the C-Cl stretching region ( $500$ – $750 \text{ cm}^{-1}$ ) are sufficiently different to permit identification of virtually all chlorinated hydrocarbons.

In Table I, we have compiled a list of spectral peaks for many species of interest in the combustion of chlorinated hydrocarbons. The list is in ascending order of wavenumber, a form convenient for the assignment of unknown spectral peaks. The naturally occurring isotopes of chlorine (which occur in a ratio of 3.09 to 1) often split bands into a number of components, depending on the number of chlorine atoms in the molecule; this splitting can be used to confirm features attributed to chlorinated compounds. Gas-phase spectra of stable  $\text{C}_1$ – $\text{C}_3$  chlorinated hydrocarbons in the  $650$ – $1350\text{-cm}^{-1}$  region are available as supplementary material. We have also included spectra of other species of interest for combustion studies. The partial pressure of the compound is included, as well as a list of prominent spectral features, which include wavenumbers of Q-band transitions and maxima in P and R branches when these bands are resolved. The measurements were made on our spectrometer with  $0.25\text{-cm}^{-1}$  resolution, a 2.28-m path length, and a total pressure of 100 Torr.

**Quantitative Measurements.** Once a given species is identified, we usually want to know its concentration in the mixture. The concentration is determined by measuring the fraction of the radiation absorbed by an unknown sample and comparing it with the absorption of samples of known concentration of the same species. Because many species are present over a wide range of concentrations, it is desirable to be able to predict the absorption strength for a particular band. The absorption of a molecular

species is assumed to follow Beer's law:

$$A = \log (I_0/I) = Ecl$$

where  $A$  is the absorbance,  $I/I_0$  is the fraction of transmitted radiation at a given wavelength,  $E$  is the species absorption coefficient,  $c$  is the species concentration, and  $l$  is the path length through the sample cell. The implication is that absorbance should be proportional to the product of the species concentration and the path length. While this equation is often used for the peak absorbance of a species, it is strictly valid only when the frequency-dependent absorption coefficient is used. Then the integrated absorbance over the band will be a constant. However, as most measurements using FTIR spectrometers are made with peak intensities, we will also use them in the following discussion.

Obtaining quantitative measurements using FTIR can be rather difficult, especially for complex gas mixtures. We [and others (23–25)] have found that in practice Beer's law behavior is often not observed. Deviations from Beer's law are observed when there are molecular associations, when systems having a very narrow line or banded structure are probed with broad-band radiation, or when bandwidths change with temperature and pressure (22). These conditions are often fulfilled when FTIR spectrometers are used to measure combustion products. We have found that the measured absorbance of a species is a function of many parameters, including concentration, total pressure, instrument operating parameters, and sample cell design.

We noted that Beer's law predicts that the absorbance of a molecular species should be proportional to the product of its concentration and path length, referred to here as the optical density. Figure 2 presents absorbance versus optical density for specific peaks of CO and  $\text{CO}_2$ , respectively. Absorbances are clearly nonlinear. It should be noted that we observed nonlinear behavior at low optical densities, as well as the expected deviations at high values. In general, smaller molecules with large rotational constants and having isolated rotational lines narrower than the spectrometer resolution exhibit this type of nonlinear behavior. Parts a and b of Figure 3 show absorbance versus optical density for propane and ethyl chloride, which have spectra consisting of broad overlapping lines. These species were found to have absorbances that increased linearly with optical density, although all would begin to go nonlinear for absorbances approaching a magnitude of 1.0. Even when Beer's law behavior was not observed, changing the path length was found to have the same effect as a proportional change in concentration.

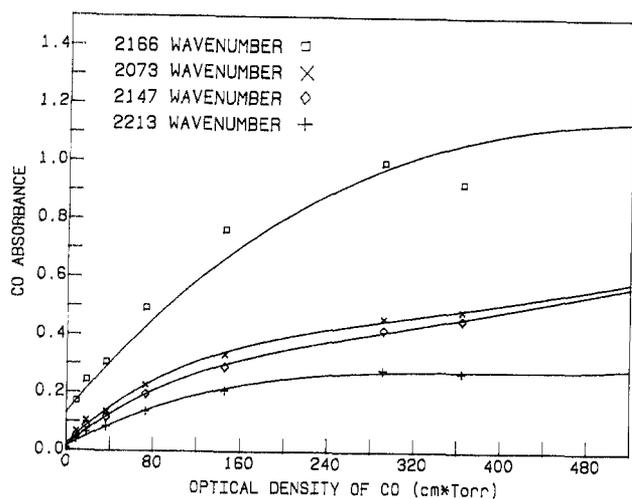
The theory of pressure broadening of absorption bands is well documented in the literature (25, 26). As total pressure is increased some molecules will absorb radiation further from the center of a rotational peak and the absorption line will broaden. Since the integrated absorbance is a constant, the peak absorbance will decrease as the pressure is raised. Experimentally, however, we found the opposite result in some cases. Figure 4 shows the effect of total pressure on the absorbance of carbon monoxide. The pressure of the carbon monoxide was 0.17 Torr (optical density  $38.8 \text{ cm} \cdot \text{Torr}$ ); nitrogen was then added to bring the total pressure to 100 Torr and then to 760 Torr. The differences in peak absorbance are dramatic. Similar behavior was noted for other species having narrow rotational lines that do not overlap, such as HCl,  $\text{CO}_2$ , and  $\text{CH}_4$ . A much weaker dependence of absorbance on total pressure was found for larger species having broad overlapping absorption spectra. For example, propane peak absorbance decreased less than 10% for a total pressure change from 0.2 to 100 Torr.

**Table I. List of Spectral Features in Chlorinated Hydrocarbon Combustion**

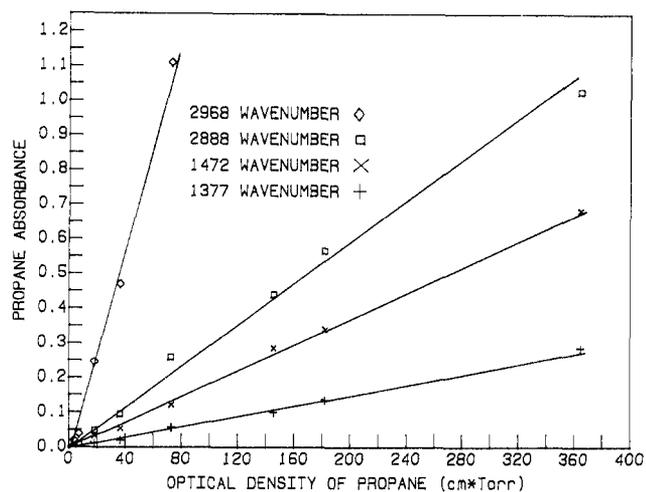
wavelength, cm <sup>-1</sup>	species	spectral type		comments
589.6	ethylene	Q		
667.1	ethyl chloride	Q	PQR	
667.6	carbon dioxide	Q	PQR	
677.1	ethyl chloride	Q	PQR	
685.5	hexachloroethane		broad peak	
695.8	<i>cis</i> -1,2-dichloroethylene	Q	PQR	
721.3	vinyl chloride	Q	PQR	
720.8	carbon dioxide	Q	PQR	
723.1	1,1,1-trichloroethane		broad peak	728-720
728	ethylene dichloride		broad peak	733-722
729.3	acetylene		twin peaks	731.0 and 729.1
731.5	1,1-dichloroethane	Q	PQR	
732.5	methyl chloride	Q (weak)	PQR	
744.2	1,1,2-trichloroethane		broad peak	747-737
750	nitrogen dioxide			
758.5	dichloromethane		double peak	764.2 and 749.7
772	chloroform		broad peak	777-770
781.9	tetrachloroethylene			
783.0	trichloroethylene	Q	PQR	
785.2	ethyl chloride	Q	PQR	
791.0	hexachloroethane		broad peak	792-790
793.9	carbon tetrachloride		broad peak	
795.8	1,1-dichloroethylene	Q	PQR	
801.4	tetrachloroethylene		broad peak	
824.6	ethane		broad peak	
826	<i>trans</i> -1,2-dichloroethylene		broad peak	832-820
850	trichloroethylene		double peak	849.5 and 850.7
857	<i>cis</i> -1,2-dichloroethylene		double Q branch	858.5 and 856.8
858.5	<i>trans</i> -1,2-dichloroethylene	Q	PQR	
869	1,1-dichloroethylene		double Q branch	868.7 and 869.4
896.6	vinyl chloride	Q	PQR	
898.6	<i>trans</i> -1,2-dichloroethylene	Q	PQR	
917	tetrachloroethylene		broad peak	921-913
937.3	1,1,2-trichloroethane	Q	PR	
940	trichloroethylene		twin peaks	944.5 and 934.7
942.3	vinyl chloride	Q	PQR	
949.6	ethylene	Q	PQR	
973.2	ethyl chloride	Q	PQR	
1020.2	methyl chloride			
1033.5	formaldehyde	Q	PQR	
1086.2	1,1-dichloroethylene			
1087.4	1,1,1-trichloroethane		double peak	1095.5 and 1087.5
1095.2	1,1-dichloroethylene		first of double peak	
1097.4	1,1-dichloroethylene		second of double peak	
1200.6	<i>trans</i> -1,2-dichloroethylene	Q	PQR	
1209.3	1,1,2-trichloroethane	Q	PQR	
1220.7	chloroform		twin peak	1220.7 and 1219.4
1232.2	ethylene dichloride	Q	PQR	
1264.4	1,1,2-trichloroethane	Q	PQR	
1268.4	dichloromethane	Q	PQR	
1288.8	ethyl chloride	Q	PQR	
1292.5	ethylene dichloride	Q	PQR	
1304.8	<i>cis</i> -1,2-dichloroethylene		double Q branch	1304.9 and 1303.4
1305.0	methane	Q	PQR	
1355.2	methyl chloride	Q	PQR	
1384.8	1,1,1-trichloroethane	Q	PQR	
1386	ethyl chloride	Q	PR	
1443	ethylene	Q	PQR	Q multipeaked
1447.6	ethyl chloride	Q	PQR	
1459.8	methyl chloride	Q	PQR	
1472.7	ethane		broad peak	
1611.2	vinyl chloride	Q	PQR	
1618	nitrogen dioxide			
1746.0	formaldehyde	Q	PQR	
1843	nitrogen monoxide			
1889.3	ethylene	Q	PQR	
2143.1	carbon monoxide	Q	PR	
2348.2	carbon dioxide	Q	PR	
2781.5	formaldehyde		sharp peak	
2779.0	formaldehyde		sharp peak	
2880	hydrogen chloride	Q	PR	
2944.4	ethyl chloride	Q	PQR	
2954.0	ethane		sharp peak	highest pt in C-H str
2966.3	methyl chloride	Q	PQR	
2988.9	ethylene	Q	PQR	
3015.8	methane	Q	PQR	

The reason for this behavior is that the very narrow rotational lines are actually optically thick and apparent absorbance is a convolution of the instrument resolution

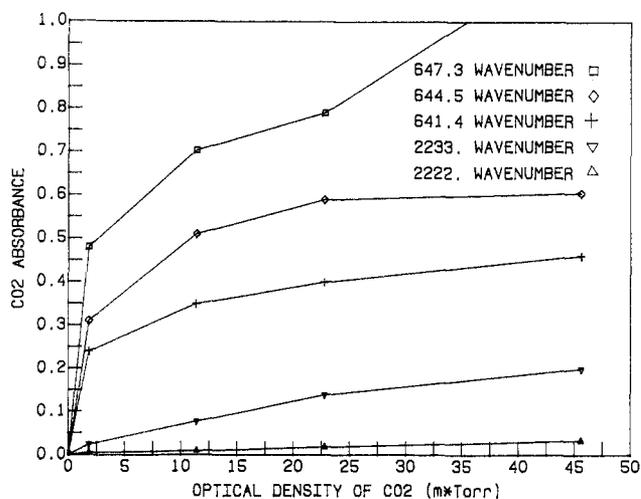
function and the line shape. As the lines are broadened with increasing pressure, more radiation is absorbed by molecules away from the center of the peak while the



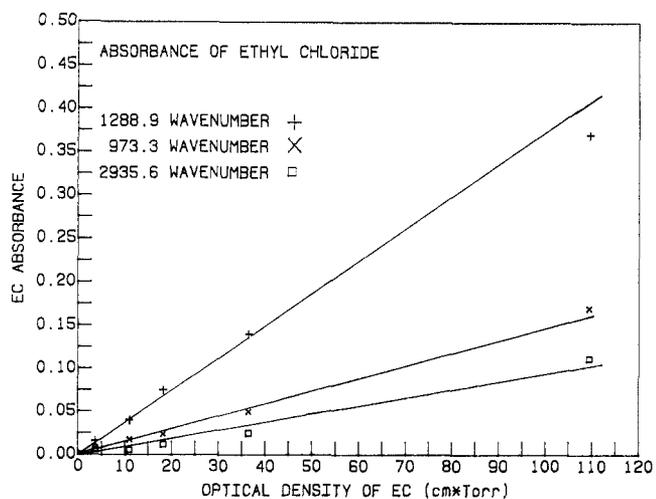
(a)



(a)



(b)



(b)

**Figure 2.** Absorbance of several spectral peaks as a function of optical density for carbon monoxide and carbon dioxide.

center continues to absorb essentially all of the incident radiation. Since the lines are not fully resolved by the spectrometer, absorption of additional radiation in the wings of the narrow line, but still within the instrument resolution, results in a higher apparent absorbance. By reducing the concentration of the absorbing species or the path length to a point where the line centers are no longer saturated, the peak absorbances do not change with a change in total pressure, as long as their line widths remain smaller than the spectrometer's resolution. Peak absorbances also decrease with increasing pressure when the line widths become greater than the instrument resolution. Reducing the CO concentration eventually resulted in an optical density where the lines were no longer saturated and peak absorbances were independent of total pressure. This occurred at an optical density of between 0.5 and 1.5  $\text{cm}\cdot\text{Torr}$ . Note that for a path length of 20 m, this corresponds to a CO pressure of only  $5 \times 10^{-4}$  Torr! A decrease in absorbance with increasing pressure was not seen because the line width remained narrower than the spectrometer's resolution.

As expected, spectrometer operating conditions have a strong effect on the peak absorbance of many species, as well as the signal to noise level. The magnitude of the effect depends on the effective resolution of the instrument compared with the width of the absorption band, with larger changes seen for very narrow bands. The actual

**Figure 3.** Absorbance of several spectral peaks as a function of optical density for propane and ethyl chloride.

resolution of a spectrometer, defined by Rayleigh's criterion, for example, can be influenced by additional factors such as an aperture in the beam path or mirrors in a particular external cell.

A sample of 0.17 Torr HCl diluted in 100 Torr nitrogen was scanned as a function of operating conditions. The collision-broadened line width (fwhm) for HCl at 100 Torr and 298 K is approximately  $0.02 \text{ cm}^{-1}$  (27). When the resolution defined by the mirror travel distance was changed from 2.0 to  $0.25 \text{ cm}^{-1}$ , the peak absorbance for each vibration-rotational band changed by a factor of 5. The signal to noise ratio is also greater for the high-resolution case, allowing a lower detectability limit. This effect of resolution on absorbance was similar for other molecules having narrow lines, such as CO and  $\text{CO}_2$ , as well as for sharp Q branches of larger molecules, such as ethyl chloride.

An aperture can be used to spatially limit the radiation emitted by the source. A smaller aperture reduces signal strength by reducing the amount of radiation that reaches the detector, but it increases actual resolution by reducing beam divergence (28). An adjustable aperture is a feature of many spectrometers. The effect of resolution and aperture setting on the absorbance of two HCl lines is shown in Figure 5. The aperture blocked 80.6% of the beam. The resolution displayed on the abscissa is the selected spectrometer resolution, not the actual resolution,

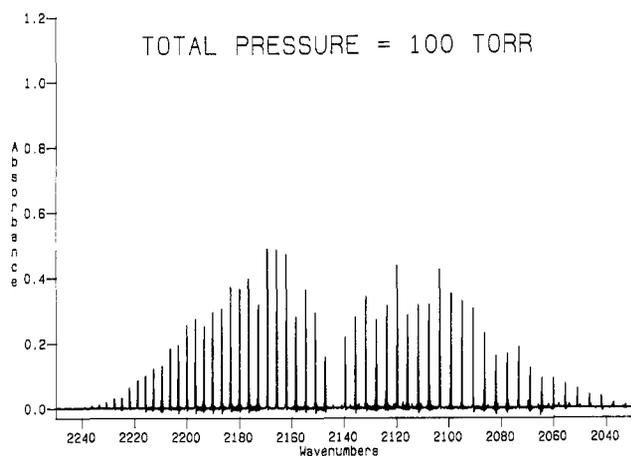
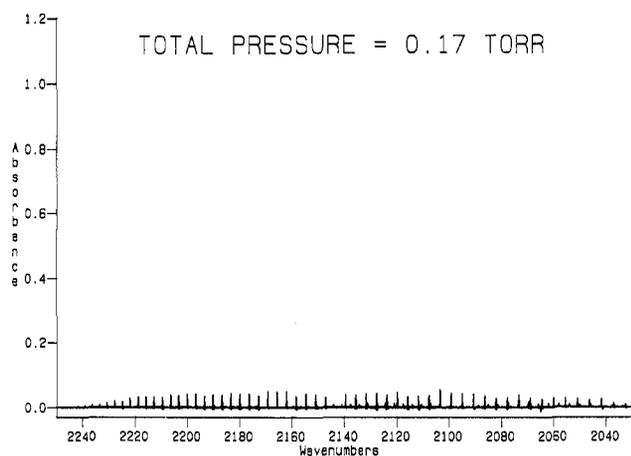


Figure 4. Effect of total pressure on CO absorbance.

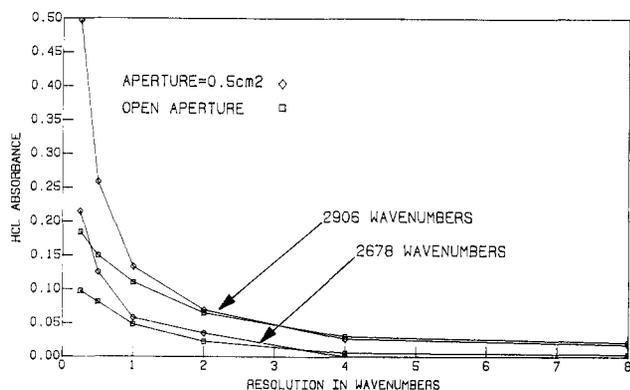


Figure 5. Effect of resolution and aperture size on HCl absorbance.

which is a function of aperture size. The important point is that at high resolutions, small apertures can have a pronounced effect on absorbance when the line width of the absorbing species is small compared to the instrument resolution. Note that added optical components, such as the mirrors used in a multipass cell, can produce the same effect if they are not properly matched to the infrared beam.

The recorded absorbances were also found to be sensitive to the alignment of the spectrometer beam splitter. Spectra of carbon monoxide taken with the beam splitter properly aligned and with the beam splitter out of alignment such that the interferogram signal was reduced 38% resulted in CO peaks that were ~16% lower for the misaligned beam splitter.

It should be obvious that quantitative measurements using FTIR systems cannot be done blindly, without re-

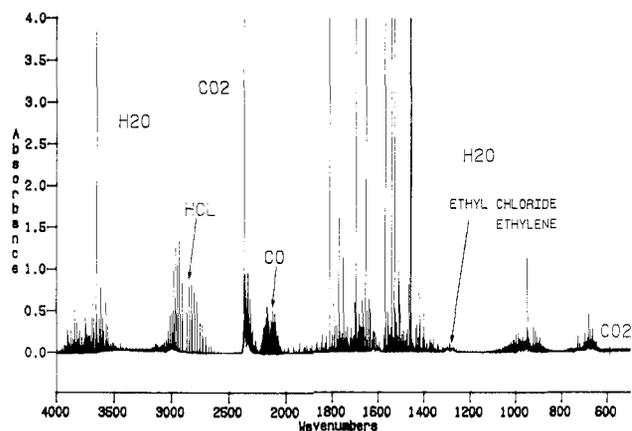


Figure 6. Spectrum of combustion products from flow reactor with ethyl chloride injection, normalized by using background of combustion products without ethyl chloride injection.

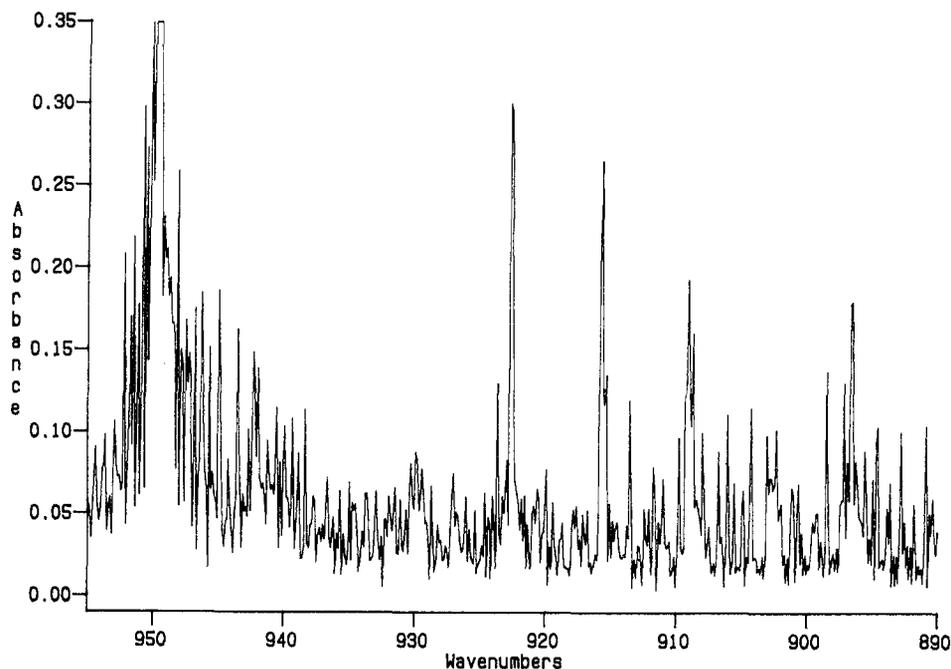
gard to the particular species being examined and the factors that affect instrument performance. Packaged spectroscopy programs must be used with care, and it is important to avoid extrapolations to conditions different from well-controlled calibration experiments.

Trade-offs must be made when selecting FTIR spectrometer operating conditions. With higher resolution comes greater data acquisition and manipulation time, larger data file size, and the added cost of a high-resolution spectrometer. A smaller aperture size gives higher resolution at the expense of signal strength. Increasing the number of scans per spectrum increases the signal to noise ratio by the square root of the number of scans at the expense of data acquisition time (28). The final example is the use of a cooled MCT detector, which improves signal to noise by more than a factor of 3 (29) but is expensive and requires liquid nitrogen.

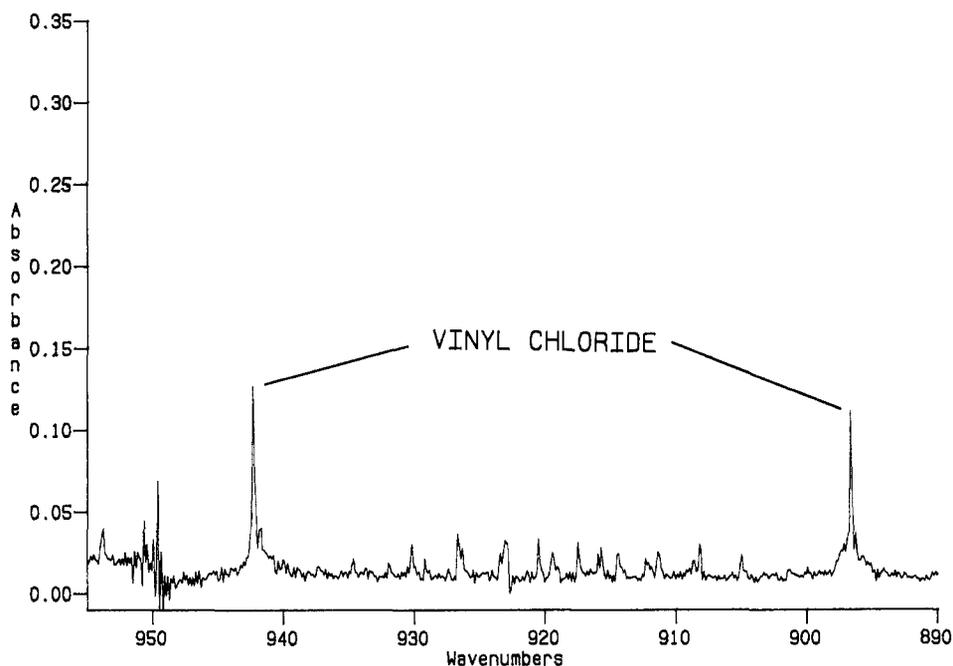
#### Chlorinated Hydrocarbon Combustion

The most prominent features of spectra of combustion products are the strong absorptions from water and carbon dioxide. Figure 6 is a spectrum of combustion products taken from the reactor while approximately 1% ethyl chloride by mass was being injected. The sample was taken 1.4 m downstream from the point of ethyl chloride injection. The equivalence ratio was 0.4, and the center-line temperature in the reactor was 1050 K. A 2.28-m path length,  $0.25\text{-cm}^{-1}$  spectrometer resolution, and 16 scans were used. The absorbance spectrum was calculated by using a background of combustion products without the injection of ethyl chloride; this highlights changes due to the chlorinated hydrocarbon reactions and greatly reduces the water and  $\text{CO}_2$  interference in the spectrum. In those regions where the absorption of light is essentially complete, however, background normalization does not improve detectability.

To detect trace species, careful subtraction of known species must be done. An example of this is shown in Figure 7. Figure 7a is the  $890\text{--}955\text{-cm}^{-1}$  portion of a spectrum taken from the reactor during ethyl chloride incineration. Numerous peaks due to ethylene are evident. Figure 7b shows the same region after a spectrum of pure ethylene was subtracted. Two peaks due to vinyl chloride, which were previously unnoticed, become clearly visible. The ethylene concentration is 1200 ppm, while the vinyl chloride concentration is determined to be 90 ppm. The formation of vinyl chloride was unexpected in the incineration of ethyl chloride and illustrates the power of infrared absorption spectroscopy (30). Often multipoint regression analysis is used to obtain the best fit of cali-



(a)



(b)

**Figure 7.** (a) Spectrum of combustion products from flow reactor with ethyl chloride injection before subtraction of ethylene. (b) Spectrum of combustion products from flow reactor with ethyl chloride injection after subtraction of ethylene.

bration spectra of several species to the sample (31). This technique, however, works only when all of the species in a spectrum have been identified.

The use of chlorinated compounds causes additional complications due to HCl formation. Measuring HCl quantitatively is difficult because of its tendency to stick to surfaces. We found it to have a strong affinity for stainless steel, as have others (32). Heating the sample lines was found to be important in reducing wall losses due to condensation. HCl is also very corrosive, particularly if water is allowed to condense in its presence. The SiO-coated silver mirrors in the long path cell were quickly and badly damaged when condensation occurred in the presence of HCl. Interestingly, the infrared signal was only

attenuated ~20%, but the HeNe laser used to align the mirrors for multiple passes could not be used. Some of the damage was apparently due to HCl that had absorbed onto particulate matter and settled on the mirrors. A 15- $\mu$ m filter placed in the sample line appeared to reduce the problem. In addition to the mirror damage, the  $3/16$ -in. stainless steel sample lines used to withdraw samples from the reactor developed pinhole leaks along their lengths.

#### Conclusions

FTIR spectroscopy is a powerful tool for measuring most combustion species. Chlorinated products of combustion are readily detectable since the C-Cl stretch region lies in a part of the spectrum away from the large H<sub>2</sub>O and CO<sub>2</sub>

interferences. We have successfully identified and quantified many species in samples of combustion products. The technique, however, cannot be used without careful consideration of spectral conditions for each species to be measured. Several calibration spectra must be examined to ensure correct quantitative analysis, and large extrapolations should be avoided.

Absorbances of species having rotational lines narrower than the instrument resolution did not adhere to Beer's law. A cell with an adjustable path length is desirable to minimize the number of calibration samples needed.

Absorbances of species having rotational lines narrower than the instrument resolution can increase with increasing total pressure for a constant partial pressure of the absorbing species. This is due to saturation of the lines within a spectral region smaller than the instrument resolution. At very low optical densities, absorbances became independent of total pressure as the lines moved from saturation.

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#### Supplementary Material Available

Gas-phase spectra of stable C<sub>1</sub>-C<sub>3</sub> chlorinated hydrocarbons and other species of interest for combustion studies (21 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24x reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, authors' names, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$37.00 for photocopy (\$39.00 foreign) or \$10.00 for microfiche (\$11.00 foreign), are required.

**Registry No.** Ethylene, 74-85-1; ethyl chloride, 75-00-3; carbon dioxide, 124-38-9; hexachloroethane, 67-72-1; *cis*-1,2-dichloroethylene, 156-59-2; vinyl chloride, 75-01-4; 1,1,1-trichloroethane, 71-55-6; ethylene dichloride, 107-06-2; acetylene, 74-86-2; 1,1-dichloroethane, 75-34-3; methyl chloride, 74-87-3; 1,1,2-trichloroethane, 79-00-5; nitrogen dioxide, 10102-44-0; dichloromethane, 75-09-2; chloroform, 67-66-3; tetrachloroethylene, 127-18-4; trichloroethylene, 79-01-6; carbon tetrachloride, 56-23-5; 1,1-dichloroethylene, 75-35-4; ethane, 74-84-0; *trans*-1,2-dichloroethylene, 540-59-0; formaldehyde, 50-00-0; methane, 74-82-8; nitrogen monoxide, 10102-43-9; carbon monoxide, 630-08-0.

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