ABSTRACT

CATALYTIC OXIDATION OF CHLORINATED HYDROCARBONS OVER POWDERED TRANSITION METAL OXIDE

by
Sanmei Xu

This study addresses the ability of powdered transition metal oxides such as manganese oxide, iron oxide and copper oxide to catalytically oxidize low concentrations of chlorinated hydrocarbons with air. The catalytic oxidation of trichloroethylene and dichloromethane in a tubular reactor system was evaluated experimentally as a function of temperature and space velocity. Gas chromatography with electron capture detector and flame ionization detector was used for quantitative analysis of feed and product streams. Gas chromatography/mass spectrometry and gas chromatography/Fourier transform infrared spectroscopy were used to identify all oxidation products. The results indicate that over 99% conversion of trichloroethylene is achieved at 915 K over fresh iron oxide, 96% conversion of trichloroethylene is achieved at 970 K over fresh copper oxide and 74% conversion of dichloromethane is achieved at 700 K over fresh manganese oxide. The major products from the oxidation of trichloroethylene over iron oxide are CO_2, Cl_2 and HCl, with trace amounts of CCl_4, C_2Cl_4 and CO.

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OVER POWDERED TRANSITION METAL OXIDE

by
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This thesis is dedicated to my dear parents

ACKNOWLEDGMENT

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CHAPTER 1

INTRODUCTION

Chlorinated hydrocarbons are widely used in dry cleaning and degreasing operations, organic chemicals manufacturing, automotive painting, etc. These materials can present environmental hazards in a number of different ways. Chlorinated hydrocarbons emitted into the atmosphere affect stratospheric ozone and when disposed in the ground can cause water pollution which affects human health, because many chlorocarbons are carcinogenic. Chlorinated hydrocarbons are very stable and are recycled when economically feasible. However, when their concentration is so low that it is not economical to recycle, then it is necessary to adsorb on granular activated carbon (GAC) in the 20 ppm range, and use high temperature incineration to destroy the chlorinated hydrocarbons in the 1000 ppm range. As a consequence of using high temperatures, expensive materials of construction and additional fuel are needed. Environmental consequences of incineration include the formation of acid gases such as NO_x and undesirable by-products such as dioxins. As a consequence of all these factors, conventional incineration is less desirable than catalytic oxidation for treating industrial exhaust streams containing 1000 ppm chlorinated compounds. At very low chlorocarbon concentrations (ca., 20 ppm) GAC adsorption is the most economical control technology.

Catalytic oxidation is a combustion process in which the chlorinated hydrocarbons in an air stream are preheated and passed through a catalyst bed usually containing metal oxides or noble metals. The catalyst promotes the oxidation at lower temperatures than required for thermal incineration (Palazzolo, 1987).

The object of this research is to improve the understanding of the fundamentals of catalytic oxidation processes for chlorinated hydrocarbons. This includes studying the effect of catalyst type, the physical parameters of catalyst, kinetic parameters for catalytic

destruction of trace levels of chlorinated hydrocarbons, the product distribution of catalytic oxidation of trace levels of chlorinated hydrocarbons, the effect of different space velocities and temperatures.

Since some chlorinated hydrocarbons contain more chlorine atoms than hydrogen atoms, they produce chlorine gas in addition to the more desirable hydrogen chloride. Hydrogen chloride is easily scrubbed in an alkaline medium. A desirable research objective is therefore to find a means of introducing additional hydrogen in order to convert all the chlorine to hydrogen chloride. We have examined the possibility of supplying the additional hydrogen required with the feed in the form of water. At elevated temperatures, chlorinated molecules acquire hydrogen atoms (either directly from a hydrocarbon molecule, or from hydrogen atoms residing on the catalyst surface, or even directly form water) to achieve production of hydrogen chloride. The carbon atoms of the chlorinated molecule are essentially converted to carbon dioxide.

CHAPTER 2

BACKGROUND

2.1 Review of the Literature

Chlorinated hydrocarbons (CHCls) are widely used in dry-cleaning and in degreasing operations, and as solvents in the pharmaceutical industry, but their vapors are toxic to human beings because of damage they cause to the liver (Bond, 1973). Dichloromethane (DCM) and trichloroethylene (TCE) were used in this research as representative solvents used in industry.

In recent years, TCE has been discovered in ground water and in aquifers used for potable water throughout the United States. It has become the subject of extensive governmental regulations and a target chemical in perhaps hundreds of environmental litigation's (Schaumburg, 1990). These two compounds, according to "Hazardous Substance Fact Sheet" (NJ Dept. Health, 1986), may be cancer causing agents in humans. There may be no safe level of exposure for a carcinogen, so all contact should be reduced to the lowest possible level.

Catalytic oxidation is an energy efficient method of destroying chlorinated hydrocarbons (Lester, 1990). Such a process involves contacting the waste gas stream with a catalyst in the presence of excess oxygen at a temperature below about 600 °C. The destruction of chlorinated hydrocarbons by thermal incineration occurs at temperature of at least 1100 °C (Bose, et al., 1983; Senkan, et al., 1986; Lee, et al., 1990). Therefore, there is a need for a catalyst which can oxidize chlorinated hydrocarbons at lower temperatures. However, the chlorine can react with the catalytic metal and poison it.

Numerous metal catalysts have been evaluated for their potential for oxidizing hydrocarbons and chlorocarbons. These metals are usually divided into noble metal catalysts and transition metal catalysts. Metal oxide catalysts for oxidation processes

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normally consist of oxides of Group VB through IB of the periodic table. As a general rule, these catalysts are more poison-tolerant than supported noble metals, though they are also somewhat less active for oxidation reactions, especially on a per metal atom basis. Metal oxide catalysts can, in principle, be prepared as either bulk oxides of uniform composition or can be supported on high surface area substrates such as γ-Al_2O_3 which also provide a high specific surface area for the metals. The relative activity of metal oxide catalysts for the complete oxidation of chlorinated compounds was summarized by Ramanathan, et al., (1989) as follows:

Co, Cr > Mn > Cu > Ni > Pt > V > Mo
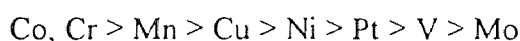
Simons, et al., (1968) considered the temperature at which 50 percent of the reactant is converted into CO_2 + CO at a particular set of flow conditions to be a characteristic measure of the activity of a catalyst. This measure allows a convenient comparison of the various metal oxide catalysts. Their data show that the temperature for 50 percent conversion to CO_2 + CO increases in roughly linear fashion with the heat of reaction Qo, defined as:

$$MO_n \longrightarrow MO_{n-1} + 1/2\ O_2\ -Qo \tag{1}$$

The corresponding equation for chlorination is:

$$MCl_n \longrightarrow MCl_{n-1} + 1/2\ Cl_2 -Qo \tag{2}$$

A comparison of equation 1 for oxidation with chlorination in equation 2 is provided in Table 1 (Shaw, 1993).

According to this mechanism, one would expect MnO_2, PdO, and V_2O_5 to be among the best metal oxides for destruction of hydrocarbons and possibly chlorocarbons. It is important to note that Cu and Fe catalysts, which have particularly good oxychlorination activity are among those having the lowest metal chloride bond energies (Satterfield, 1980).

Table 1 Bond Energies of Catalytic Materials

	Equation 1		Equation 2
	M-O, kcal/mol		M-Cl. kcal/mol
Co_3O_4	38	Co_2Cl_5	28
Cr_2O_3	NA	$CrCl_3$	40
CuO	34	$CuCl_2$	17
Fe_2O_3	54	$FeCl_3$	15
MnO_2	17	$MnCl_4$	NA
NiO	58	$NiCl_2$	38
PdO	20	$PdCl_2$	23
SnO_2	70	$SnCl_4$	23
TiO_2	69	$TiCl_4$	51
V_2O_5	29	VCl_5	29
ZnO	83	$ZnCl_2$	50

NA = Not Available

Yao (1984) looked at CuO as an automotive exhaust catalyst for ethanol oxidation. They evaluated CuO catalysts (on γ-Al_2O_3, α-Al_2O_3, ZrO_2, and CeO_2/ γ-Al_2O_3) using a simulated exhaust gas of 1% O_2 and 0.14% ethanol (in helium). CuO/ γ-Al_2O_3 had the highest activity, as measured by the lowest temperature required to produce no detectable ethanol in the exit gas. Copper catalysts are also subject to deactivation by chlorine. Ostrovoskii, et al., (1987) discovered that deactivation was irreversible and was due to interaction of Cu with chlorine compounds. Earlier work has reported extensively on the characteristics of the Deacon process (HCl + O_2 = Cl_2 + H_2O), where copper-based catalysts are extensively deactivated by volatilization of $CuCl_2$ at the temperatures employed, normally around 600 °C (Satterfield, 1980).

Some studies have involved noble metal catalysts to treat chlorinated hydrocarbon compounds. U.S. patent 1,485,375 (Bond, 1973) showed that 0.8 to 1.5 wt % Pt on γ-Al_2O_3 catalysts are effective in treating a number of chlorinated compounds, such as CH_2Cl_2, CCl_4, $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4, and have good performance in the presence of propane. The percent destruction of chlorinated compounds is above 95% but the selectivity to HCl was not investigated.

Pope, et al., (1978) studied the oxidation of 1,1,1-trichloroethane in a mixture of gases over a platinum-honeycomb catalyst. They compared the destruction efficiency of a Co_3O_4 catalyst with a Pt catalyst. The Co_3O_4 catalyst was observed to be the more effective in the presence of chlorinated fuels. Hung, et al., (1989) showed that a Cr_2O_3/Co_3O_4 binary catalyst performed better than a Pt catalyst in the catalytic oxidation of CH_3Cl and CH_2Cl_2 in the presence of propane. The product distribution as a function of temperature was not investigated.

Some investigators evaluated transition metal oxides catalysts on supports. A chromium oxide impregnated catalyst on a support was used in the oxidation of chlorinated compounds which treated CH_3Cl (Senkan, et al., 1986), 1,1-dichloroethane (Ramanathan, et al., 1989), hexachlorobenzene and hexachlorobutadiene (Johnston, 1976), and PCB's (Novinson, 1989). It was shown that Cr_2O_3 catalysts have good activity for chlorinated compounds destruction. In a study by Ramanathan, et al., (1989), the selectivity to chlorine from catalytic oxidation of 1,1-dichloroethane was determined to be 50% at 500 °C.

Young (1982) investigated the oxidation of methylene chloride over a commercial 12.5 wt % chromia/alumina catalyst. Young reports a significant increase in CO content, and decrease in CO_2 content, of the exit gas over time, though this is not related to any observable change in catalyst composition, e.g., halogen or carbon disposition on the catalyst. It is postulated, however, that chloride or perchlorate formation may occur on the catalyst. The addition of water inhibited the formation of Cl_2 and heavier (than methylene

chloride) chlorinated hydrocarbons, which were observed in the absence of added water vapor in the inlet gas. However, the addition of water, by itself, does not affect selectivity to oxides of carbon, $CO + CO_2$. Michalowicz (1982) examined the oxidation of a series of chlorinated ethylenes on 12.5 wt % Cr_2O_3/alumina and Cr_2O_3/silica (chromia content not given) among other catalysts. On the chromia/alumina catalyst, the formation of chlorinated hydrocarbon polymers was observed both downstream of the catalyst and presumably on the catalyst as well in the oxidation of trichloroethylene. This is said to be formed by the reaction of Cl_2 formed in the oxidation reaction with an undefined "chlorinated trichloroethylene". The addition of water to the inlet gas increased both the conversion and CO_2 yield and produced less polymers. Further increase in water content of the inlet gas (resulting in a hydrogen/chlorine atomic ratio of 2.94) caused essentially complete conversion and no polymer formation.

Hydrated nickel oxides, manganese oxides, cobalt oxides (Lavanish, et al., 1976; Sare, et al., 1977) and titania catalysts (Tanguay, 1989) were evaluated for the catalytic oxidation of C_2-C_4 halogenated hydrocarbons and dichloromethane. Conversions of 45 to 90 percent were obtained for vinyl chloride (VCM), vinylidene chloride (VDCM) and trichloroethane over the nickel oxides (II) and (II and III). At temperatures over 450 °C, nickel oxide catalysts started to deactivate by thermal sintering. For an initial concentration of 46.5 ppm of VCM or VDCM at 107 °C, Lavanish showed that 99% conversion was obtained with the cobalt oxide (II) catalyst. Cobalt oxides (II) catalysts deactivated by reacting with Al_2O_3 support to form $CoAl_2O_4$ at temperature over 850 °C. The destruction of CH_2Cl_2 on titania catalyst showed poor activity (Tanguay, 1989).

A catalyst's overall effectiveness depends on the selectivity for products from practical detoxification. Previous research in the heterogeneous catalytic oxidation of low concentrations of chlorinated hydrocarbons with air has focused on identifying highly active catalysts and final reaction products at temperatures high enough to achieve

essentially complete oxidation. In general, reaction conditions are chosen that result in complete oxidation to H_2O, CO_2 and HCl.

Several companies have commercialized new VOC catalysts. Allied-Signal has reported success in catalytically oxidizing chlorinated hydrocarbons, but has not released details. Its patent cites platinum, vanadium pentoxide, and titanium dioxide as major catalyst constituents. ARI international uses a chromic oxide catalyst in a fluidized bed to eliminate chlorinated hydrocarbons, but this system releases fine particles of chromium that may pose an environmental problem. Dedert-Topsoe manufactures a proprietary commercial metal oxide catalyst for destroying chlorinated materials and KSE has developed an experimental proprietary catalyst for the same purpose (Farrauto, 1992).

Dibble and Raupp (1990) reported photochemical oxidation of trichloroethylene to hydrochloric acid and carbon dioxide using titanium dioxide catalysts irradiated with ultraviolet light. But more work is needed to determine the commercial feasibility of this process.

Although chlorinated hydrocarbons in waste water are usually removed by air-stripping (air is forced through the waste water to take up the hydrocarbons), a competitive approach is to treat them directly in the liquid phase. A catalytic hydrodechlorination method that yields chloride-free hydrocarbons and hydrochloric acid is being developed by Suphan Kovenklioglu (1992) at Stevens Institute of Technology in collaboration with Engelhard. Kovenklioglu and coworkers use precious-metal catalysts supported on carbon carriers to gain high conversion efficiencies and selectivities at room temperature in both batch and trickle-bed reactors.

2.2 Basic Principles of Catalysis

2.2.1 General Description of a Catalyst

The basic concept of a catalyst is that of a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process. A catalyst cannot

change the ultimate equilibrium determined by thermodynamics; its role is to accelerate the rate of approach to equilibrium. Many commercial heterogeneous catalysts are composed of an active material and a support. The active component is normally a metal or metal oxide, and the support is a ceramic or metal monolith. Molecules vary in size and chemical structure. So, different catalysts are necessary for different reaction processes. The optimization of a catalyst is specific for each reaction and requires selection of appropriate operating condition. Therefore, determination of performance of a catalyst is dependent on empirical results.

2.2.2 Catalytic Processes and Kinetic Characterization

In a catalytic process, reactants must interact with the "active site" on the catalyst, the term "active site" is thought to be that site (or sites) on the catalyst surface in which chemisorption and reaction occur. Basically, a catalytic process includes: (Augustine, 1988; Du, 1990)

1. Bulk diffusion: reactants must pass through stagnant film from the gas or liquid phase.

2. Pore diffusion: reactants diffuse or are transported through pore structures to active sites.

3. Chemisorption: a reactant chemically adsorbs on active sites i.e., by bonding.

4. Chemical reaction: a reactant is converted to a product on the active sites.

5. Desorption: products desorb from the active sites.

6. Product diffusion: products diffuse through pores from the active sites.

7. Product diffusion: products diffuse through the film to the bulk gas or liquid phase.

Steps 1 and 7 are controlled by mass transfer limitation; steps 2 and 6 are controlled by pore diffusion limitations; and steps 3, 4 and 5 are controlled by chemical

reaction limitations. The physical and chemical properties of catalysts and operating conditions that control the rate of reaction are carefully chosen.

Much research is required to optimize the properties of a catalyst and the conditions for its practical use. The effect of rate limiting phenomena is correlated with the Arrhenius expression from which activation energies are determined.

A general plot depicting the three rate regimes in catalysis is shown in Figure 1. Figure 2 illustrates a conversion versus temperature profile. The relationship used in plotting Figure 1, normally ln k versus 1/T, is determined from the Arrhenius expression as follows:

$$k = A \exp(-Ea/RT)$$

$$\ln k = \ln A + (-Ea/R) * (1/T)$$

Where,   k = rate constant,

A = preexponential constant,

Ea = activation energy (kcal/mole),

R = gas constant (kcal/mole * K),

T = absolute temperature (K).

The calculation of the activation energy, Ea, from the slope of the Arrhenius plot allows an assessment of the rate limiting step. From Figures 1 or 2, it is evident that reactions controlled by chemical kinetics are most sensitive to temperature, while mass transfer controlled reaction are essentially temperature independent.

2.2.3 Catalyst Deactivation

A catalyst may lose its activity or its selectivity for a wide variety of reasons. The causes may be grouped loosely into:

1. Poisoning

2. Fouling

3. Reduction of active area by sintering or migration

Mass Transfer Control
E < 4 k cal/mole

Pore Diffusion Control
E >= 4-8 k cal/mole

Chemical or Kinetic Control
E >= 8 k cal/mole

lnk

1/T (K)$^{-1}$
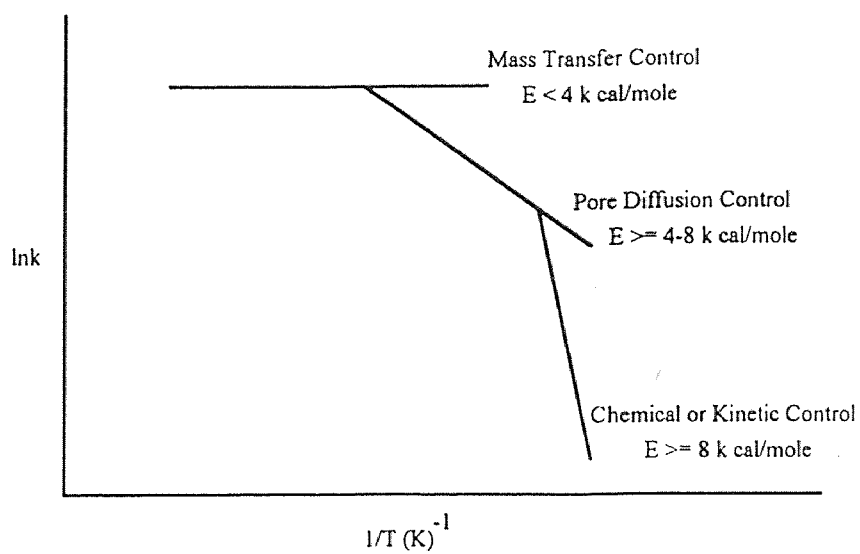
Figure 1 Arrhenius equation in catalytic processes

CONVERSION vs TEMPERATURE

MASS TRANSFER

CONVERSION

PORE DIFFUSION

CHEMICAL REACTION
OR KINETIC CONTROL
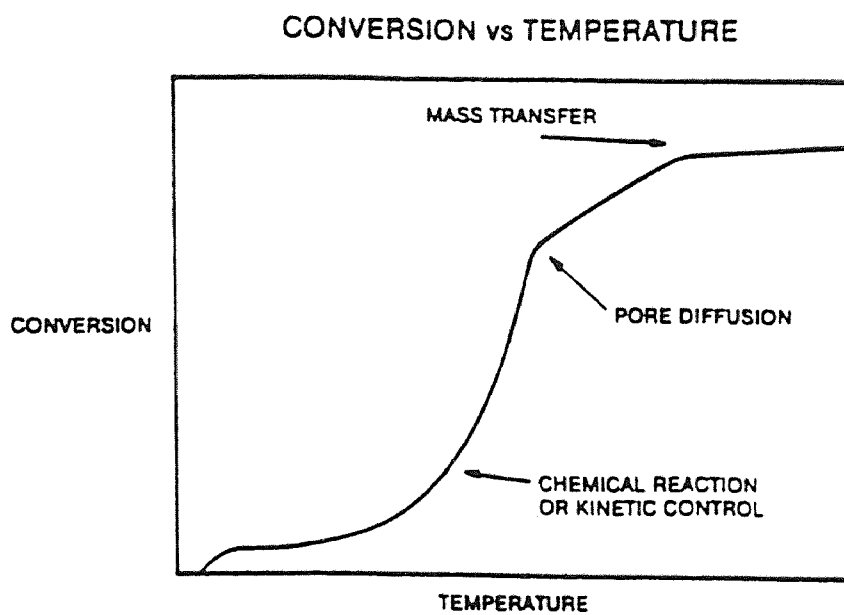
TEMPERATURE

Figure 2 Conversion of reactant as a function of temperature
showing rate controlling regions

4. Loss of active species

A catalyst poison is a chemical present in the feed stream that interferes with the normal operation of the catalyst, reducing its activity. In the oxidation of chlorinated hydrocarbons, a catalyst can easily be poisoned by chloride. It may poison a metal by forming a surface metal chloride, or it may enhance sintering via the formation of volatile metal chlorides (Satterfield, 1980).

Therefore, development of a chloride tolerant catalyst or additives which can react with the chloride, thus avoiding catalyst poisoning is an important aspect for catalytic oxidation of chlorinated hydrocarbons.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 Catalyst Materials

The catalysts used in this research were purchased from Cerac, incorporated. Those Catalysts were supplied as powder catalysts.

Iron (III) Oxide, Fe_2O_3

-100 mesh.

Typically 99.999% pure

Lot Number X14439

CAS # 1309-37-1

Density 5.24 (gm/cm^3)

Melting Point 1565°C

Copper (II) Oxide, CuO

-200 mesh

Typically 99.9% pure

Lot Number X12542

CAS # 1317-38-0

Density 6.4 (gm/cm^3)

Melting Point 1326°C

The manganese (IV) oxide catalyst used in this research were purchased from Strem Chemicals, Inc. These catalyst was supplied as powder catalyst.

Manganese (IV) Oxide, MnO_2

-325 mesh

BET Surface Area 112 m^2/g

Apparent Diameter 7.1 μm

Bulk Density 1.06 g/cm^3

Theoretical Density 5.03 g/cm^3

Melting Point 535°C

3.2 Experimental Apparatus

The experiments are based on a laboratory - scale tubular reactor system as shown in Figure 3. This system consists of a 2.5 cm inside diameter quartz tube reactor (Kontes Scientific Glassware, Inc.) residing in a vertical three zone controlled furnace (Applied Test System, Inc.) containing known volumes of powder metal oxide catalyst, the middle zone was designed to maintain a flat temperature profile over the length of the catalyst.

A glass U-tube containing dichloromethane (DCM), CH_2Cl_2 (Aldrich Chemicals, Co., 99.9%) feed in liquid form was placed in an ice-bath. The U-tube allows a portion of the air to bubble through the devise before mixing with the rest of the air and feeding the mixture to the reactor. In order to change the concentration of DCM, the split in the amount was varied into the reactant bubbler gas, with the rest of the air mixed at a junction after the bubbler. Approximately 1000 ppm trichloroethylene (TCE), C_2HCl_3 gas was mixed with the air and fed to the reactor. The concentration of TCE was changed by varying the flow rate of dilution air. The flow rate of inlet gases were measured with two calibrated rotameters (Cole Parmer Co.). The range of one rotameter is 0-10 cm^3/min, the other is 0-3000 cm^3/min.

The reactor temperatures was monitored by two 0.16 cm chromel-Alumel (K-type) thermocouples (Omega Engineering, Inc.) which were inserted in both sides of the quartz tube reactor and place in the center line immediately before and after the catalyst. Since the measured temperatures was sufficiently low, no correction was made for radiation.

The products gas was analyzed by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared spectroscopy (GC-FTIR) in order to identify the components in the product stream. Quantitative analysis was then
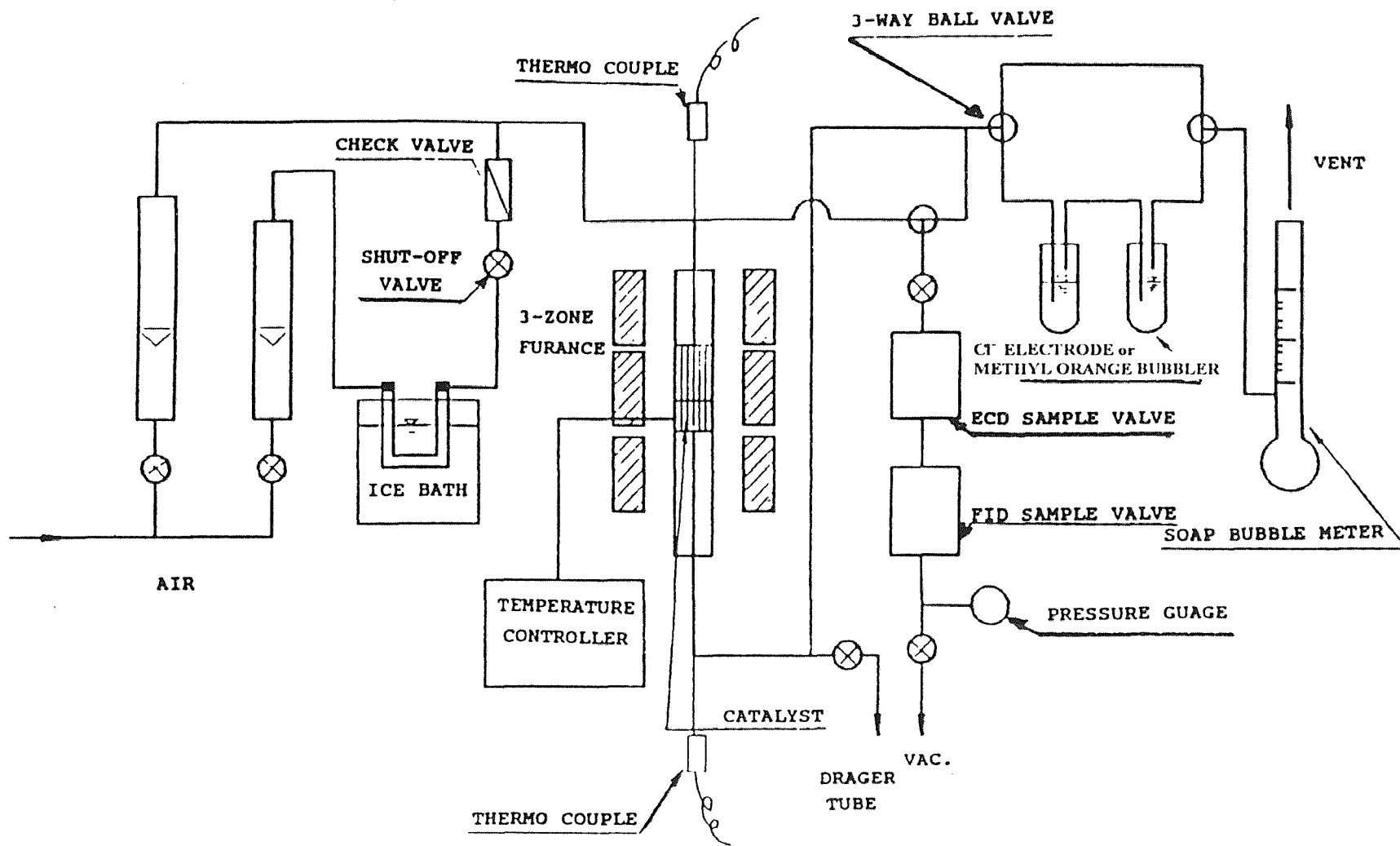
Figure 3 Schematic of catalytic oxidation system

conducted chromatographically after individual calibration of each peak. The concentration of carbon monoxide, carbon dioxide was quantitatively analyzed by gas chromatography (GC) using a nickel hydrogenation catalyst to convert these compounds to methane and measure the methane with a flame ionization detector (FID). The concentration of chlorinated hydrocarbons was quantitatively analyzed by gas chromatography (GC) with electron capture detector (ECD). The concentration of chlorine was measured by methyl orange colorimetric method. In addition, the product gas was bubbled through a scrubber to absorb hydrogen chloride and the concentration of chloride ion in the aqueous solution was measured with a chloride ion selective electrode.

The calibration and feed gases were purchased from the Matheson Co. and were used directly from cylinders in the experiments. The air which we used as feeding gas was of research grade purity zero air, with less than 5 ppm water and less than 1 ppm hydrocarbons.

3.3 Instrumental Analysis

3.3.1 Qualitative Analysis

Gas-chromatography/mass spectrometry has become one of the most powerful tools available to chemists for identifying the components of complex mixtures. A fused silica capillary column, which is installed in the GC, passes through a short, line-of-sight transfer line directly into the ion trap assembly of the mass spectrometer. Samples are injected onto the capillary column through the GC injection port. Sample molecules are then separated by gas chromatography. The effluent from the GC flows through the transfer line and is introduced into the ion trap. Upon entering the ion trap, sample molecules are ionized by electron ionization (EI). The resulting samples ions are analyzed according to their mass-to-charge ratios. The sample ions are then detected by an electron multiplier that produces a signal proportional to the number of ions detected. The ion current signal from the electron multiplier is received and amplified by the system electronics and is then passed

on to the data system for further processing and display. In this way mass spectrum of individual components, separated by the GC, are obtained.

The products from the catalytic oxidation of trichloroethylene (TCE) over iron oxide catalyst or copper oxide catalyst were collected in an empty sampling cylinder that was cleaned with acetone and distilled water and evacuated, and then analyzed by gas chromatography/mass spectrometry (Varian Saturn). The sample was separated on a 30m x 0.25mm I.D., 0.25um DB-5 capillary column (J & W. Scientific) and identified by ion trap analyzer of mass spectrometer according to their mass spectra. The GC/MS operating conditions, using the nomenclature of the instrument manufacturer, were as follows:

Capillary column: DB-5, 30m x 0.25mm I.D., 0.25um (J & W Scientific)

Carrier gas: Helium, 1 ml/min

Oven: 40 °C for 4 min, 40 °C-80 °C at 20 °C/min, 80 °C for 10 min

Injector: 1 ul, Split 1:100; 150 °C

Transfer line: 230 °C

Mass range: 40 to 350 amu

Seconds/Scan: 0.500 (2 uscans)

Acquire time: 20 minutes

Fil/Mul delay: 0 seconds

Peak threshold: 1 count(s)

Mass defect: 100 mmu/100 amu

Background Mass 39 amu

Ionization mode: EI

Auto Ion Control: ON

Cal gas: OFF

The stationary phase of DB-5 capillary column is (5%-phenyl)-methylpolysiloxane which makes DB-5 a relatively non-polar column. For chlorinated hydrocarbons, DB-5 capillary columns give very good separation and resolution. But for more polar

compounds, this column can not give an effective separation. In order to separate more polar compounds and confirm the analytical results from GC/MS, the products from catalytic oxidation of trichloroethylene were also analyzed by gas chromatography/Fourier transform infrared spectroscopy (BIO-RAD).

Coupling capillary column gas chromatography with Fourier transform infrared spectrometers provides a potent means for separating and identifying the components of difficult mixtures. Radiation form a broad-band IR source is fed through a Michelson interferometer (Griffiths, et al., 1983) which modulates the source beam. This beam is then focused onto a lightpipe which serves as interface between the column and the detector. The lightpipe is the actual IR cell (it can be thought of as a special high pressure, high temperature gas cell) in which the GC peaks are measured. It consists of a short length of capillary-glass tubing, which is gold-coated on the inner bore. IR-transmitting windows are affixed to each end, and the lightpipe is heated to prevent condensation of compounds contained in the GC effluent. The GC effluent is passed into one end of the lightpipe via a heated transfer line, and it travels down the length of the tube towards the outlet line. The IR beam, which is focused on the end of the lightpipe, travels down the lightpipe by bouncing off the gold coating on the inside of the lightpipe maximizing the path length for enhanced sensitivity while minimizing the dead volume to lessen band broadening. Any material passing through the cell will absorb IR radiation. The IR beam passes through the KBr window at the end of the lightpipe and is focused onto the IR detector. The radiation detector is a highly sensitive, liquid-nitrogen-cooled, narrow-range, mercury/cadmium telluride (MCT) detector covering the spectral range of approximately 4000-680 cm^{-1}. The detector signal is sampled at discrete intervals to produce a discrete interferogram. The interferogram is fed to the computer for Fourier transformation and further processing. In this way, IR spectra of individual components, separated by the GC, are obtained.

The products from catalytic oxidation of trichloroethylene were separated on a 30m x 0.32mm I.D., 0.5um DB-WAX capillary column (J & W Scientific) and identified by a narrow-range MCT detector of the Fourier transform infrared spectrometer according to infrared spectra of individual components. The GC/FTIR operating conditions were as follows:

Capillary column: DB-WAX, 30m x 0.32mm I.D., 0.5um (J & W Scientific)

Carrier gas: Helium, 6 ml/min

Oven: 40 °C

Injector: 5 ml, Splitless; 150 °C

Detector: FID, 250 °C Helium make-up at 25 ml/min

Air flow rate: 390 ml/min

Hydrogen flow rate: 30 ml/min

Transfer line: 250 °C

Scan Speed Selection: 20 KHZ

Delay: 3 seconds

Low pass filter: 4.5 KHZ

Collect Sensitivity: 1.5

Number of Scans: 4

Collection time: 30 min

Inject delay before saving: 0

Spectral region start: 4000

Spectral region end: 700

The stationary phase of DB-WAX capillary column is polyethylene glycol which allows DB-WAX to have unique polarity and selectivity properties. In this experiment, DB-WAX capillary column can effectively separate not only more polar inorganic compound but also chlorinated hydrocarbons.
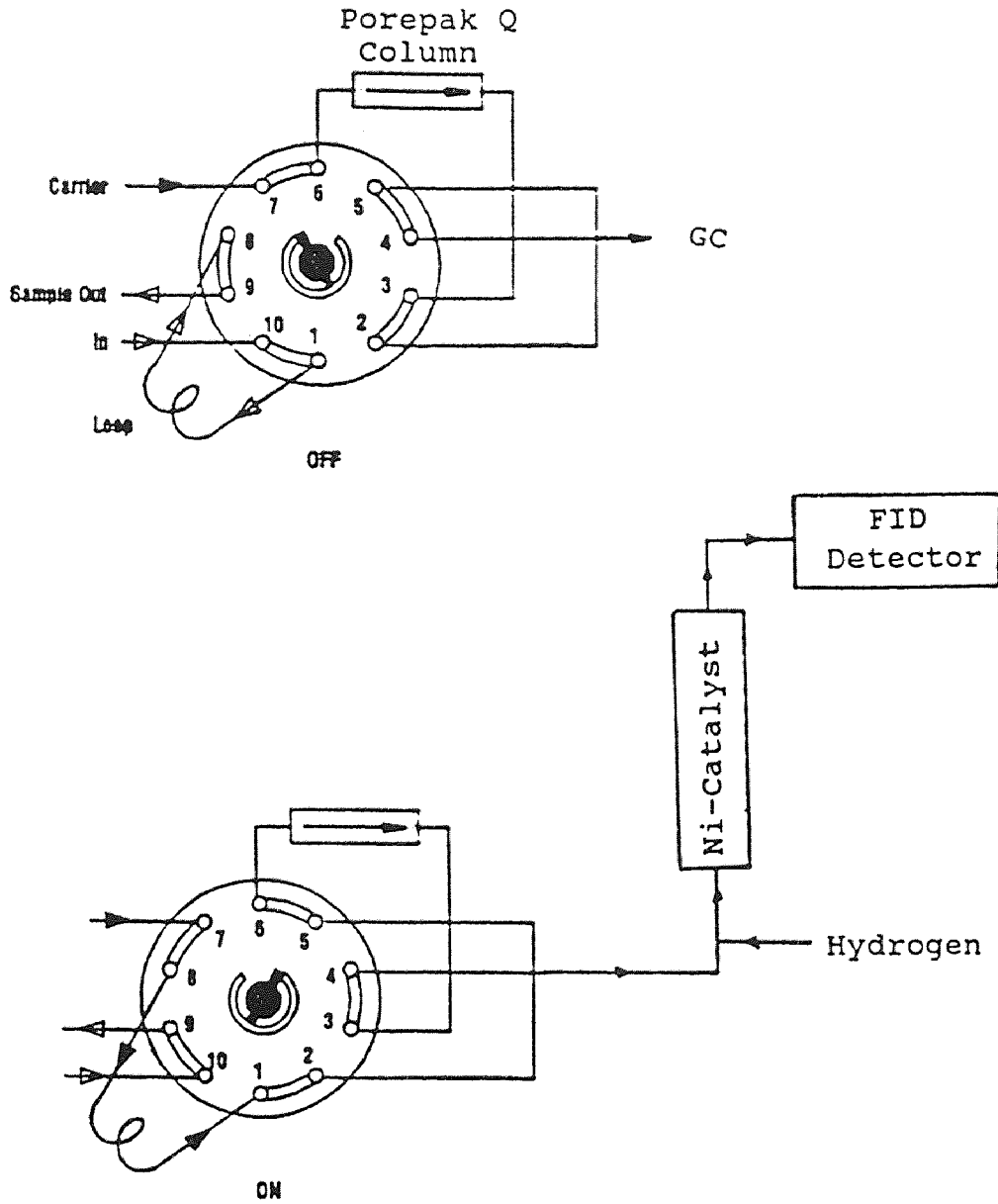
Figure 4 Nickel hydrogenation catalyst system

3.3.2 Quantitative Analysis

The on-stream analysis was conducted at 45 minute intervals by pulling part of the effluent product stream with a vacuum pump through a six points gas sampling valve, from which it was picked up by the carrier gas to either of the two on-line gas chromatographys (Hewlett Packard 5890).

The chlorinated hydrocarbons were separated on a 1/8 inch 10 feet stainless steel column packed with 80/100 mesh Chromosorb GAW and detected by electron capture detector (ECD).

The carbon monoxide, methane and carbon dioxide were separated on a 1/8 inch in diameter by 6 feet long stainless steel column packed with 80/100 mesh Poropak Q and hydrogenated over nickel catalyst system to methane before detection by flame ionization detector (FID). This was done in order to increase the sensitivity for the analysis of the oxides of carbon by orders of magnitude, and thus improve carbon balances. The flow schematic for the nickel hydrogenation catalyst systems is shown in Figure 4 (facing page 20). When the ten-point sampling valve is at the off position, the product effluents pass through the sampling loop and discharge to the hood. Once the valve is switched over to the on position, the effluents are carried out by helium from the sampling loop in to the Poropak Q column. The individual peaks are then hydrogenated with hydrogen to methane using the nickel catalyst at 350 °C. Thus, the carbon monoxide, methane and carbon dioxide peaks are detected as methane but recognized based on retention time.

All chlorinated hydrocarbons, carbon dioxide and carbon monoxide concentrations were calibrated with standard gas mixtures purchased from Matheson Co.. The calibration curve of trichloroethylene, shown in Figure 5, was made by diluting 1000 ppm trichloroethylene to five lower concentrations according to their partial pressure, and use of one purchased 116 ppm trichloroethylene mixture in air to check this calibration. Hewlett Packard 3396A integrators were used as both recorders and integrators. The GC operating conditions were as follows:
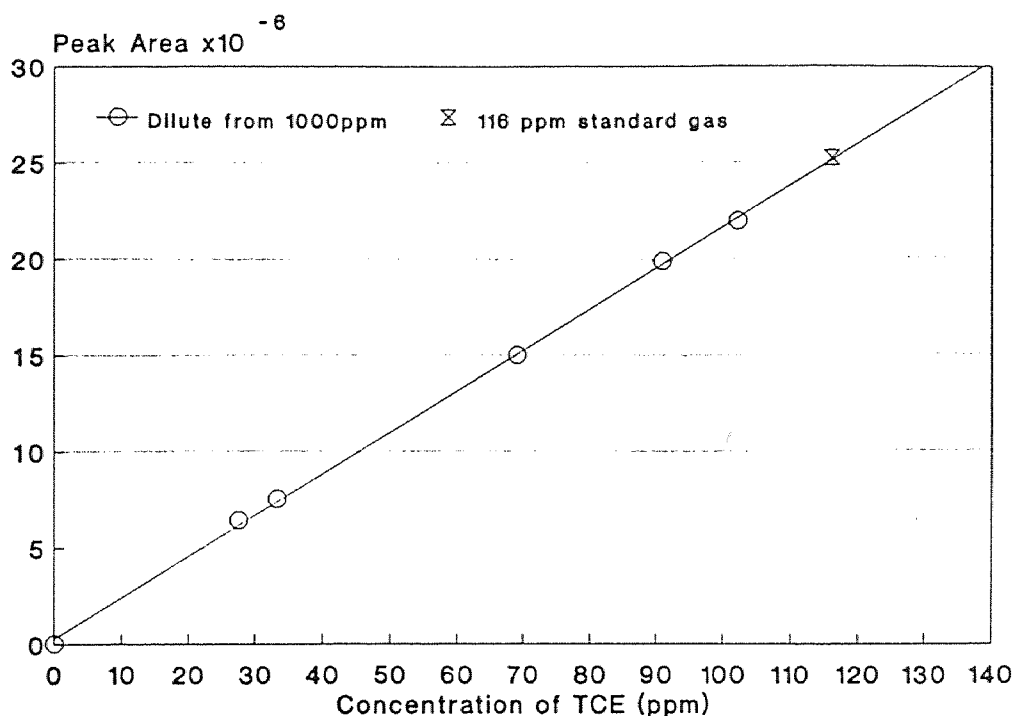
Figure 5 Calibration curve of trichloroethylene

GC one: for chlorinated hydrocarbons

Column packing materials: 2% SE 30 on GAW 80/100,

1/8"x10', ss (Alltech Associates, Inc.)

Carrier gas: Nitrogen, 30 ml/min

Oven: 40 °C for 4 min, 40 °C-80 °C at 20 °C/min, 80 °C for 10 min

Injector: 150 °C

Detector: ECD 250 °C

GC two: for methane, carbon monoxide, carbon dioxide

Column packing materials: Porapak Q 80/100, 1/8"x6' ss (Hewlett Packard)

Carrier gas: Helium, 20 ml/min

Oven: 40 °C

Injector: 350 °C

Detector: FID 250 °C

START not resol.

1.176 CH₂ Cl₂

3.321
C₂Cl₄

7.566
C₂HCl₃

STOP
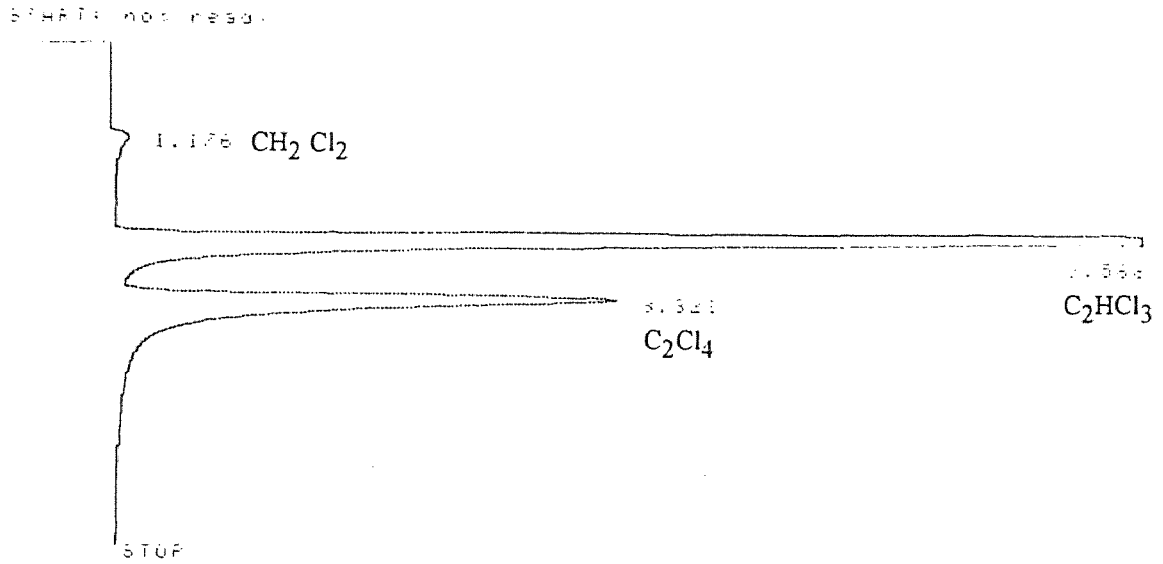
Figure 6 Peak resolution and retention time of chlorinated hydrocarbons
on ECD detector

START

1.158 CO

1.473 CH₄

3.473 CO₂

STOP

Figure 7 Peak resolution and retention time of CO, CH₄ and CO₂
on nickel hydrogenated FID detector

Air flow rate: 400 ml/min

Hydrogen flow rate: 35 ml/min
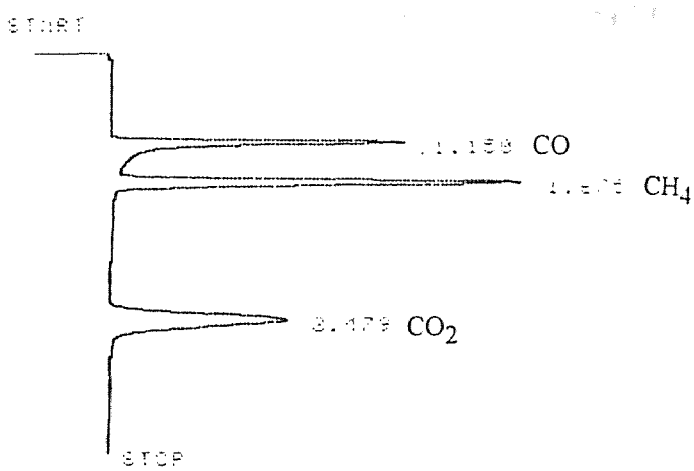
Nickel catalyst reactor: 350 °C

Figures 6 and 7 (facing page 22) show the typical peak resolution and retention times for dichloromethane, trichloroethylene and perchloroethylene on ECD detector and carbon monoxide, carbon dioxide and methane on nickel hydrogenated FID detector.

The concentration of chlorine gas was measured by methyl orange colorimetric method. This method was specific for chlorine gas and had no interferences. First, 0.06 g of methyl orange was dissolved in water and diluted to 1 liter. Several liters of pH 2 buffer solutions were also prepared. A mixture containing 5 ml methyl orange solution and 100 ml pH = 2 buffer solution was added to the bubbler shown in Figure 3. Then any product chlorine gas was bubbled through this solution. The decrease in the methyl orange color was proportional to the concentration of chlorine. The calibration curve for chlorine gas, shown in Figure 8, was made by bubbling purchased standard chlorine gas through the methyl orange solution for different periods of time. Then the solution was measured by ultraviolet spectrophotometer at wavelength 505 nm. Since the ultraviolet absorbance is proportional to the color strength of methyl orange solution. The decrease in the ultraviolet absorbance is therefore proportion to the concentration of chlorine. The concentrations of hydrogen chloride were determined by absorbing it in distilled water and the concentration of chloride ion in the aqueous solution was measured by chloride ion selective electrode. Since chlorine also dissolves in water and one chlorine produces one chloride ion. The concentration of hydrogen chloride is equal to that the total concentration of chloride ion minus the concentration of chlorine. The calibration curve for chloride ion, shown in Figure 9, was made by preparing several different concentrations of sodium chloride solutions and measuring the change in voltage of these solutions using a chloride ion selective electrode.
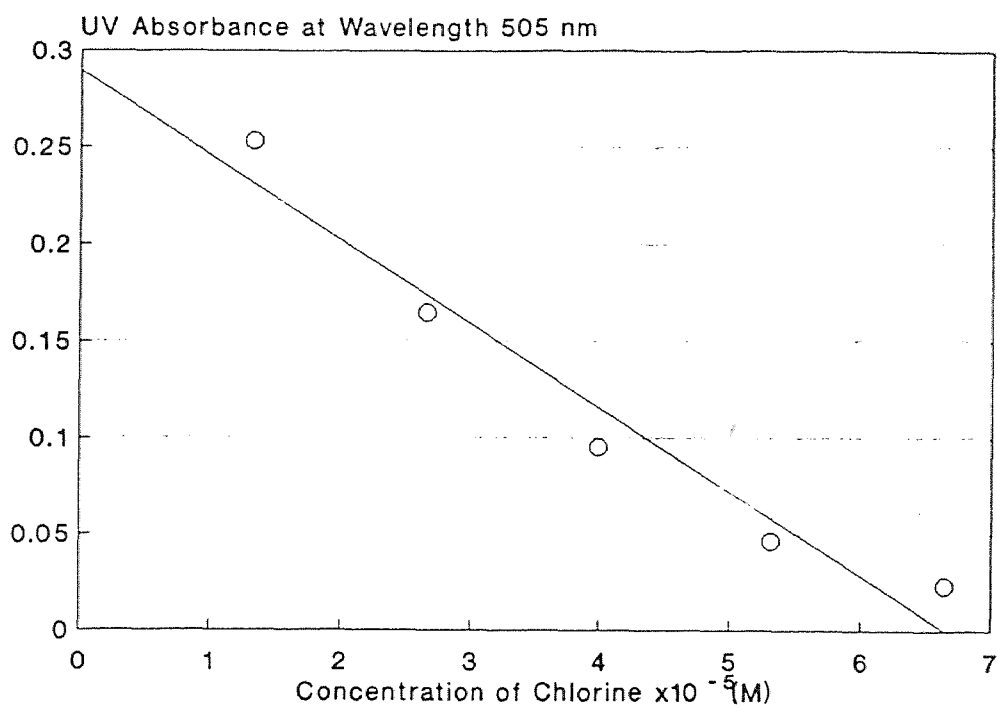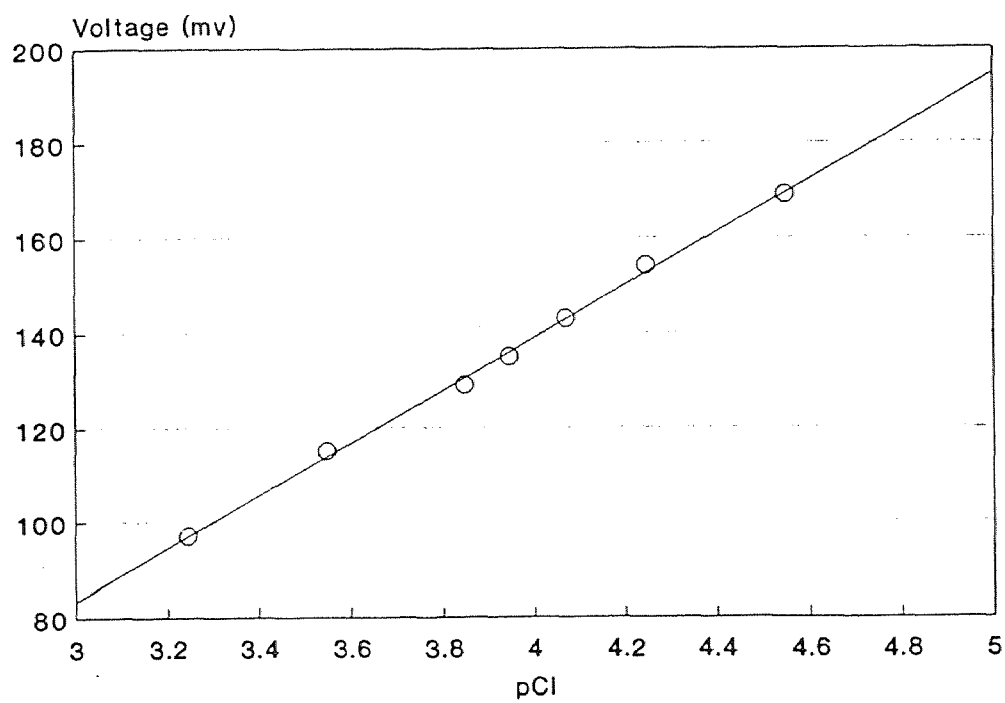
Figure 8 Calibration curve of chlorine gas

Figure 9 Calibration curve of chloride ion

3.4 BET Surface Area Measurement

The BET method measures the adsorption of nitrogen from several nitrogen/helium gas mixtures containing different partial pressures of nitrogen in the range of 0.05 to 0.35. The BET surface area was obtained by solving equation (3) with the measured adsorbed mass values.

$$\frac{1}{X\,[\,P_o/P - 1\,]} = \frac{C - 1}{X_m * C}\,\frac{P}{P_o} + \frac{1}{X_m * C} \tag{3}$$

Where: X = mass of adsorbate adsorbed at relative pressure P/P_o

P = partial pressure of adsorbate

P_o = saturated vapor pressure of adsorbate

X_m = mass of adsorbate at one monolayer coverage

C = a constant which is a function of the heat of adsorbate condensation

and heat of adsorption

The mass of a monolayer of adsorbate may be calculated from a plot of the left side of this equation vs. P/P_o. Xm and C appear in the expressions for the slope and the intercept of this straight-line plot:

slope   = $(C-1) / (X_m * C)$

intercept   = $1 / (X_m * C)$

and hence: X_m = $1 / (\text{slope} + \text{intercept})$

surface area   = $[\dfrac{X_m * 6.02 * 10^{23}}{22{,}400 \text{ cm}^3/\text{g}}] * 1.09 * [\dfrac{M}{6.02 * 10^{23} * \rho}]$

M =   molecular weight of nitrogen, $M = 28$

ρ =   density of the adsorbed molecules, nitrogen at $-195.8^{\circ}C$, $\rho = 0.808$ g/cm^3

All the samples used were weighed, inserted in a quartz U-tube. The U-tube was installed on the Altamira catalyst characterization instrument (Altamira Instruments, Inc.). Then the manual operations of BET software was followed. A standard setup for a three point BET run is as follows:

1. Treatment

2. Vapor pressure determination

3. Ambient pressure determination

4. Flow BET (10% nitrogen in helium)

5. Pulse calibration (10% nitrogen in helium)

6. Flow BET (20% nitrogen in helium)

7. Pulse calibration (20% nitrogen in helium)

8. Flow BET (30% nitrogen in helium)

9. Pulse calibration (30% nitrogen in helium)

The operating parameters of the BET run are listed in Table 2.

Table 2 Operating Parameters of BET Method

Treatment	Treatment Gas	Flow Rate	Hold Time	
	Nitrogen	30 (cc/min.)	10 min.	
Flow BET	Adsorbate Gas	Flow Rate	Adsorption Time	Desorption Time
	10 % N2 in He	20 (cc/min.)	4.0 min.	4.0 min.
BET Calibration	Adsorbing Gas	Flow Rate	Carrier Gas	Flow Rate
	Nitrogen	30 (cc/min.)	10 % N2 in He	20 (cc/min.)
Flow BET	Adsorbate Gas	Flow Rate	Adsorption Time	Desorption Time
	20 % N2 in He	20 (cc/min.)	4.0 min.	4.0 min.
BET Calibration	Adsorbing Gas	Flow Rate	Carrier Gas	Flow Rate
	Nitrogen	30 (cc/min.)	20 % N2 in He	20 (cc/min.)
Flow BET	Adsorbate Gas	Flow Rate	Adsorption Time	Desorption Time
	30 % N2 in He	20 (cc/min.)	4.0 min.	4.0 min.
BET Calibration	Adsorbing Gas	Flow Rate	Carrier Gas	Flow Rate
	Nitrogen	30 (cc/min.)	30 % N2 in He	20 (cc/min.)

CHAPTER 4

RESULTS AND DISCUSSION

This section presents the result of the research for oxidation of dichloromethane over manganese oxide powder, trichloroethylene over copper oxide powder and iron oxide powder.

4.1 Catalytic Oxidation of DCM over MnO_2

4.1.1 Catalyst and Space Velocity

The catalytic oxidation of dichloromethane was conducted over manganese oxide powder. Using 2 ml manganese oxide powder and total flow rate of 1000 ml/min, the space velocity was calculated as follows:

Space Velocity = total actual flow rate / catalyst volume

$$= (1000 \text{ ml/min} * 60 \text{ min/hr}) / 2 \text{ ml}$$

$$= 30,000 \text{ v/v/hr}$$

4.1.2 DCM Feed Concentration Measurements

The vapor pressure of different organic compounds can be calculated using the following equation (Reid, 1987):

$\ln P = A - B / (T+C)$

in which: P = vapor pressure in mm Hg at temperature T

A, B and C = empirical constants

T = temperature in K

The parameters for dichloromethane (DCM) are:

A = 16.3029 mm Hg

B = 2622.44 mm Hg * K

C = -41.70 K

At T = 273 K; P = 144.4 mm Hg

In order to obtain approximately 200 ppm feed concentration, dichloromethane in liquid form in a ice bath was carried out by 1 ml/min air, and then diluted with 1000 ml/min air. The feed concentration was estimated as follows:

Concentration = (carrier flow rate) * (P/760) / total flow rate

$$= (1 \text{ ml/min}) * (144.4 \text{ mm Hg}/760 \text{ mm Hg}) / 1001 \text{ ml/min}$$

$$= 190 \text{ ppm DCM}$$

The actual feed concentration was measured by gas chromatography at various intervals through each experiment and was in rough agreement with the estimate.

4.1.3 DCM Conversion and Materials Balance

The catalytic oxidation of dichloromethane was conducted in the temperature range of 450 to 750 K, and at the indicated space velocity of 30,000 v/v/hr and the initial concentrations of dichloromethane approximate 200 ppm. The dependence of conversion of dichloromethane on temperature is shown in Figure 10. It was found that the conversion was most sensitive to temperatures between 525 and 625 K. The conversion was least sensitive to temperatures above 700 K. This suggests that a chemical kinetics controlled zone exists in the temperature range of 525-625 K. At temperatures above 750 K, the conversion decreases from 70-80 % to 30-40 %, which implies that the MnO_2 catalyst powder may undergo physical sintering, thermal cracking, or phase fusion to form channels, which allows the reactant to bypass part of catalyst.

The materials balance for the catalytic oxidation of dichloromethane over MnO_2 catalyst was conducted at temperatures of 605 K and 663 K and at the indicated space velocity of 30,000 v/v/hr. The results are summarized in Table 3. The products are carbon dioxide, chlorine, hydrogen chloride, tetrachloromethane and chloroform. The

concentration of tetrachloromethane and chloroform decrease rapidly with increasing temperature. Table 3 also shows the excellent carbon and chlorine balances.
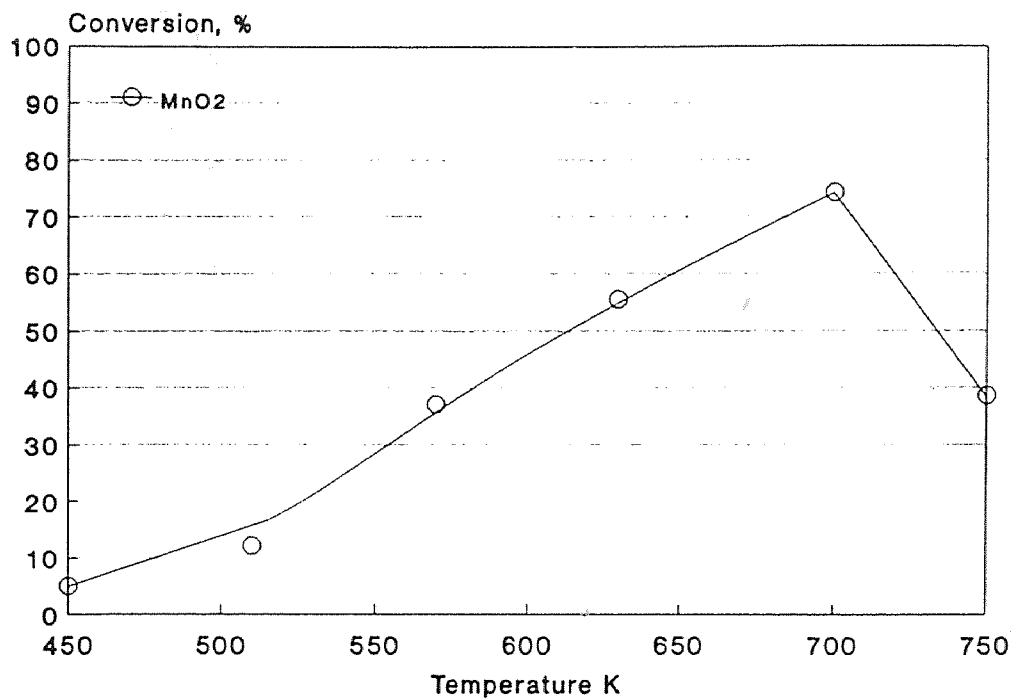

Figure 10 Conversion of 200 ppm DCM as a function of temperature over MnO_2

Table 3 Materials Balance for the Oxidation of 240 ppm DCM over MnO_2 powder

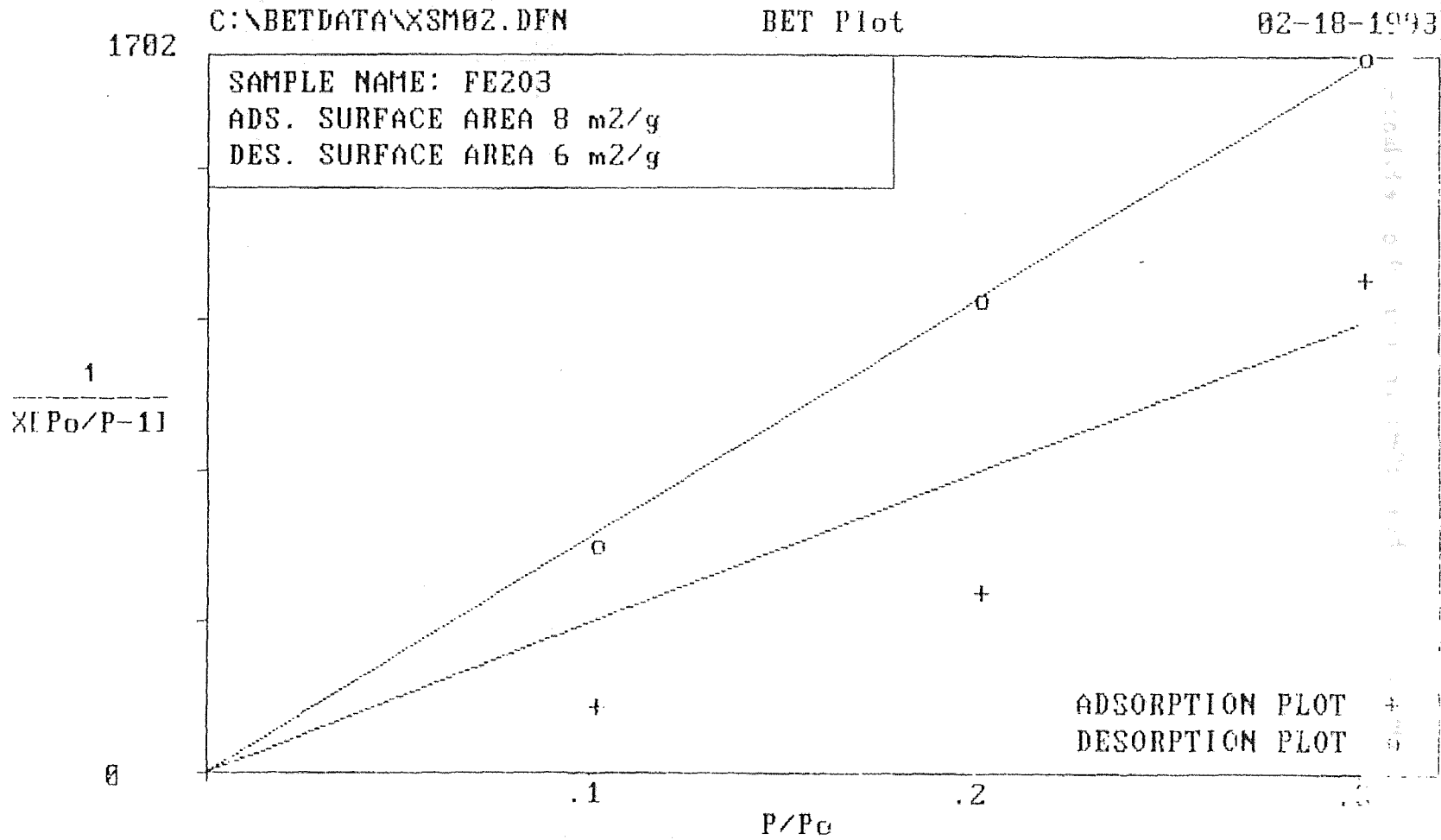| Temp.	CH2Cl2	CHCl3	CCl4	CO2	HCl	Cl2	Carbon	Chlorine
K	ppm	ppm	ppm	ppm	ppm	ppm	Balance	Balance
300	240.6	--	--	--	--	--	100	100
605	163.4	13.3	21.5	50.4	14.3	20.5	103.3±10%	105.5±10%
663	152.6	1.9	8.4	88.6	56.5	60.5	105.8±10%	109.8±10%

Figure 11 BET plot for Fe₂O₃ powder

4.2 Determination of Surface Area of Catalyst by BET Method

Weigh out 0.1873 g fresh copper oxide powder, and pour into the quartz U-tube sample cell. Place a plug of quartz wool in the top of the U-tube on the exit side to prevent blowing sample into the instrument. Install the U-tube on the Altamira catalyst characterization instrument. Follow the BET standard procedure. The operating parameters of the flow BET method were summarized in the experimental approach (page 25).

Weigh out 0.1162 g fresh iron oxide powder, and pour into the U-tube of the quartz sample cell. Measure the BET surface area of iron oxide used the same procedure and the same operating parameters as copper oxide.

In order to confirm the procedure of BET surface measurement and the operating parameters are correct, 0.0527 g fresh β-Al_2O_3 powder whose surface area is 320 m^2/g is poured into the U-tube of the quartz sample cell and its surface area is measured.

The BET plot for Fe_2O_3 powder is showed in Figure 11 (facing page 29), The BET plots for CuO powder and β-Al_2O_3 powder are showed in Figures A1 and A2 (appendix A). Because the adsorption peaks tend to be broad and tailing, the desorption surface area is always better choice. The result of β-Al_2O_3 surface area was in good agreement with a calibrated value using static BET measurements. This convinced us that the procedure for BET surface measurement and the operating parameters were correct and the results of iron oxide surface area and copper oxide surface area were correct. Therefore, the surface area of Fe_2O_3 is 6 ± 2 m^2/g and the surface area of CuO is less than 3 m^2/g.

4.3 Qualitative Analysis of the Products of Catalytic Oxidation of TCE by GC-MS and GC-FTIR

At temperature 773 K, space velocity of 6,000 v/v/hr and initial concentrations of trichloroethylene of approximately 600 ppm, the catalytic oxidation of trichloroethylene

over iron oxide catalyst was run over an hour in order to reach steady state. Then, the product stream was collected in an empty sampling cylinder. Gas chromatography/mass spectrometry and gas chromatography/Fourier transform infrared spectroscopy were used to obtain a qualitative product analysis. The operating parameters of GC/MS and GC/FTIR were summarized in experimental approach.

The chromatogram from the GC/MS analysis is shown in Figure 12. There are a total of four peaks, the separation of three chlorinated hydrocarbons is well satisfied but the inorganic compounds can not be separated by the DB-5 capillary column. The mass spectra of each peak are shown in Figures B1, B2 and B3 (appendix B). A comparison of these results with a mass spectrum of library source search showed a good match. The chromatogram from the GC/FTIR analysis is shown in Figure 13. There are a total of five peaks. As with the GC/MS analysis, three chlorinated hydrocarbons were separated well, and in this case the CO_2 and H_2O were also separated. The IR spectra of each individual components are shown in Figures C1, C2, C3, C4 and C5 (appendix C). Since Cl_2 is a homonuclear compound, no net change in dipole moment occurs during its vibrations or rotations, consequently, Cl_2 can not be detected by FTIR. The reason that CO and HCl can not be detected may be due to the low concentrations of CO and HCl at the reaction condition being investigated and the limitation of MCT sensitivity. In addition, Drager gas color-detector tubes were employed to verify the existence of hydrogen chloride and chlorine as the products in this reaction at other reaction conditions. The specific response of trichloroethylene oxidation product to nickel hydrogenated flame ionization detector, and the retention of the product matches the retention of standard carbon monoxide gas indicate the existence of carbon monoxide in the product. Therefore, the products of catalytic oxidation of trichloroethylene were carbon dioxide, carbon monoxide, hydrogen chloride, chlorine, water, tetrachloromethane and perchloroethylene.
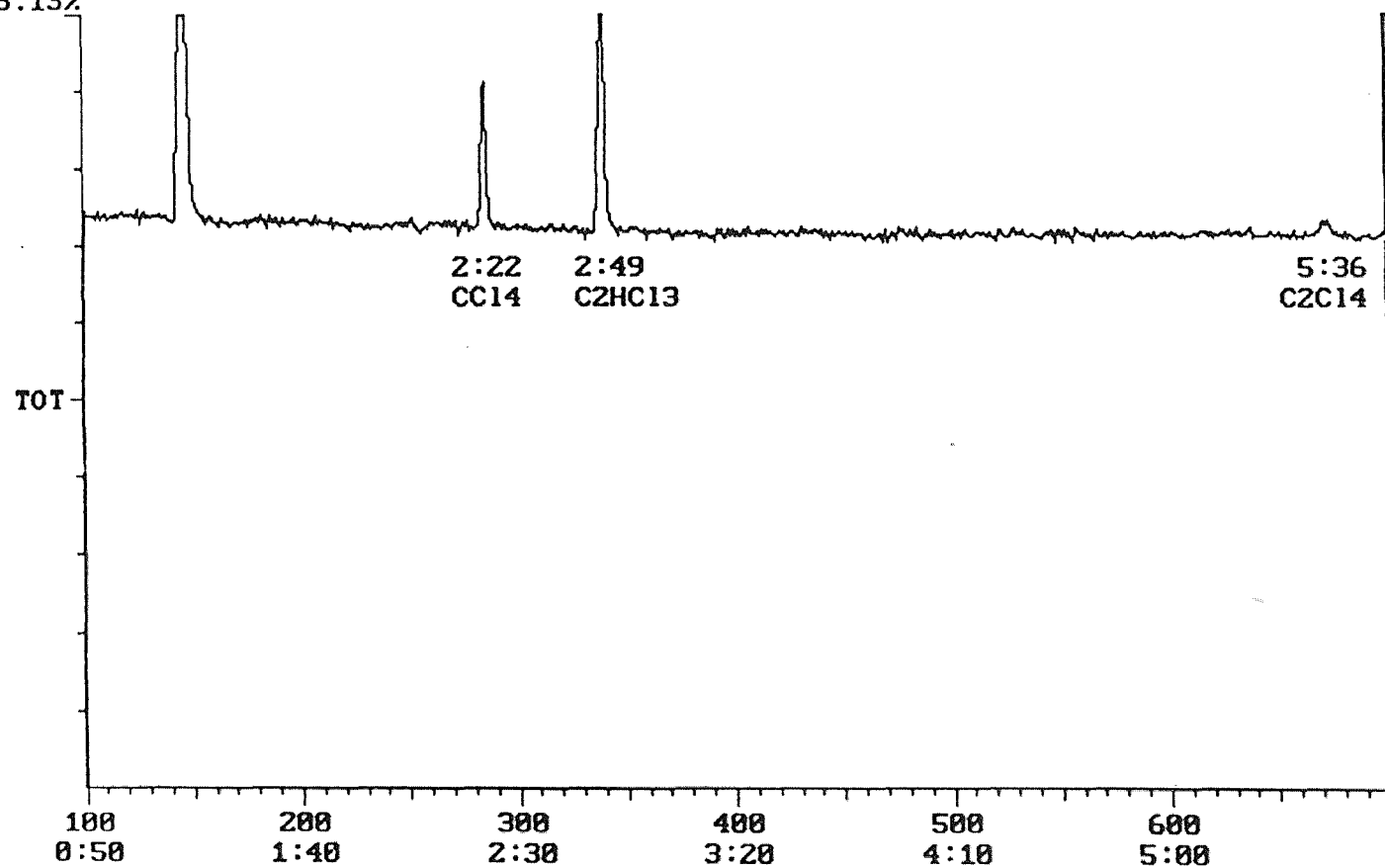
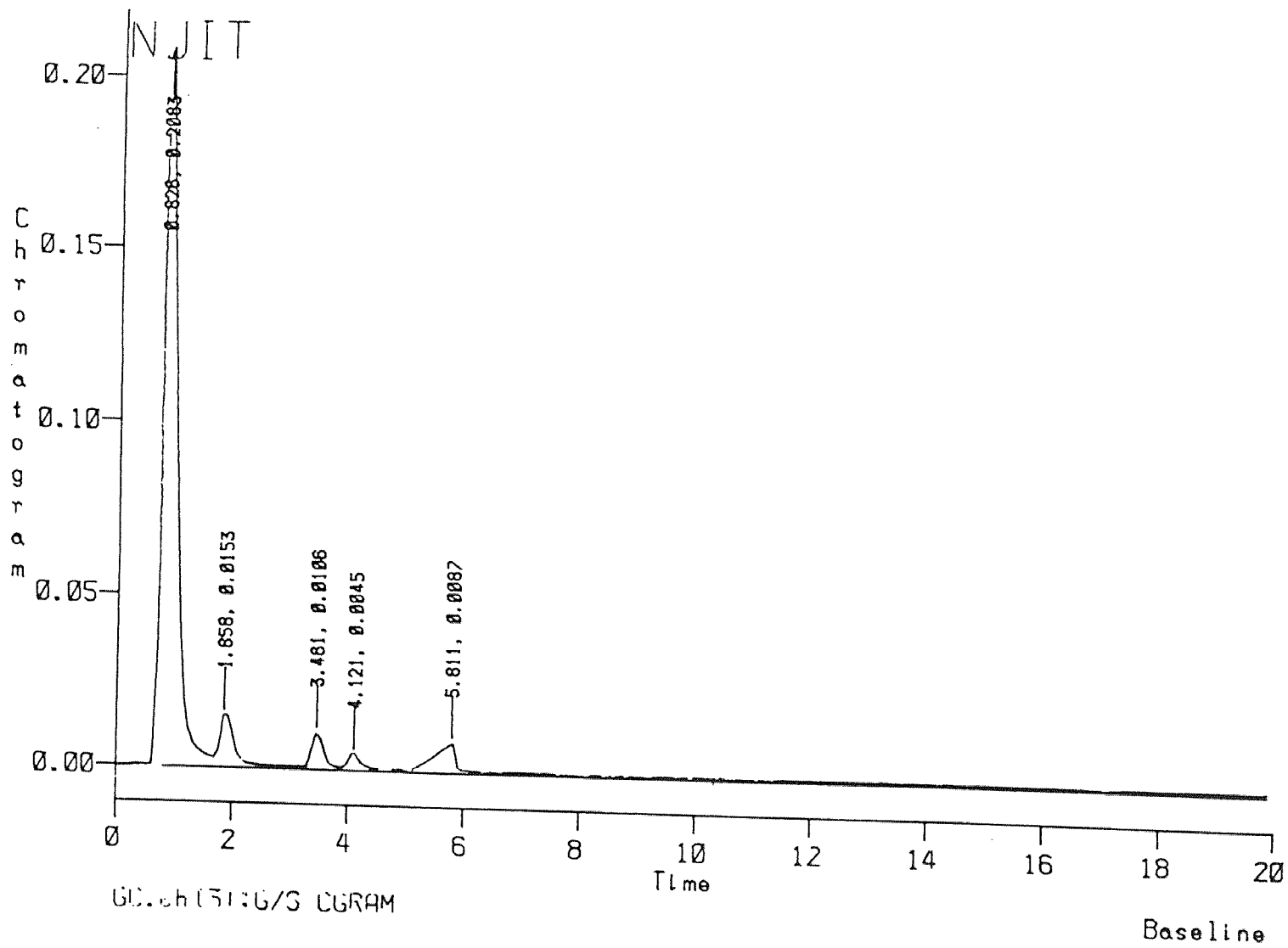Figure 12 Chromatogram of TCE oxidation products from GC/MS

Figure 13 Chromatogram of TCE oxidation products from GC/FTIR

4.4 Catalytic Oxidation of TCE

4.4.1 Catalyst and Space Velocity

The catalytic oxidation of trichloroethylene was conducted over iron oxide powder catalyst or copper oxide powder catalyst. Using a graduated cylinder to measure 2 ml metal oxide powder catalyst and total flow rate of 400 ml/min, the space velocity can be calculated as follow:

Space Velocity = total flow rate / catalyst volume

$$= (400 \text{ ml/min} * 60 \text{ min/hr}) / 2 \text{ ml}$$

$$= 12,000 \text{ v/v/hr}$$

4.4.2 Feed Concentration of TCE

In order to obtain 100 ppm trichloroethylene, 1000 ppm trichloroethylene from a gas mixture cylinder was diluted ten times with dry air. The actual concentration of trichloroethylene was measured by gas chromatography at various intervals throughout each experiment.

4.4.3 The Effect of Temperature on TCE Oxidation

At the indicated space velocity of 12,000 v/v/hr, and the initial concentrations of trichloroethylene of approximately 100 ppm, the catalytic oxidation of trichloroethylene over iron oxide catalyst was conducted in the temperature range of 475 to 975 K. The catalytic oxidation of trichloroethylene over copper oxide catalyst was conducted in the temperature range of 625 to 975 K. The dependence of conversion of trichloroethylene on temperature is shown in Figure 14. For the catalytic oxidation of trichloroethylene over iron oxide catalyst, it was found that the light-off temperature is on the order of 575 K, and the conversion is most sensitive to temperatures between 600 and 700 K. The conversion is least sensitive to temperatures above 725 K. This suggests that a chemical kinetics controlled zone exists in the temperatures 600-700 K, and a mass transfer

controlled zone occurs at temperature over 725 K. For the catalytic oxidation of trichloroethylene over copper oxide catalyst, it was found that the light-off temperature of 775 K is significantly higher than that for iron oxide, and the conversion is most sensitive to temperatures between 800 and 875 K. The conversion is least sensitive to temperatures above 975 K. This suggests that a chemical kinetics controlled zone exists in the temperatures 800-875 K, and a mass transfer controlled zone occurs at temperature over 975 K. But at a temperature above 875 K, it was found that the copper oxide catalyst had partly melted.
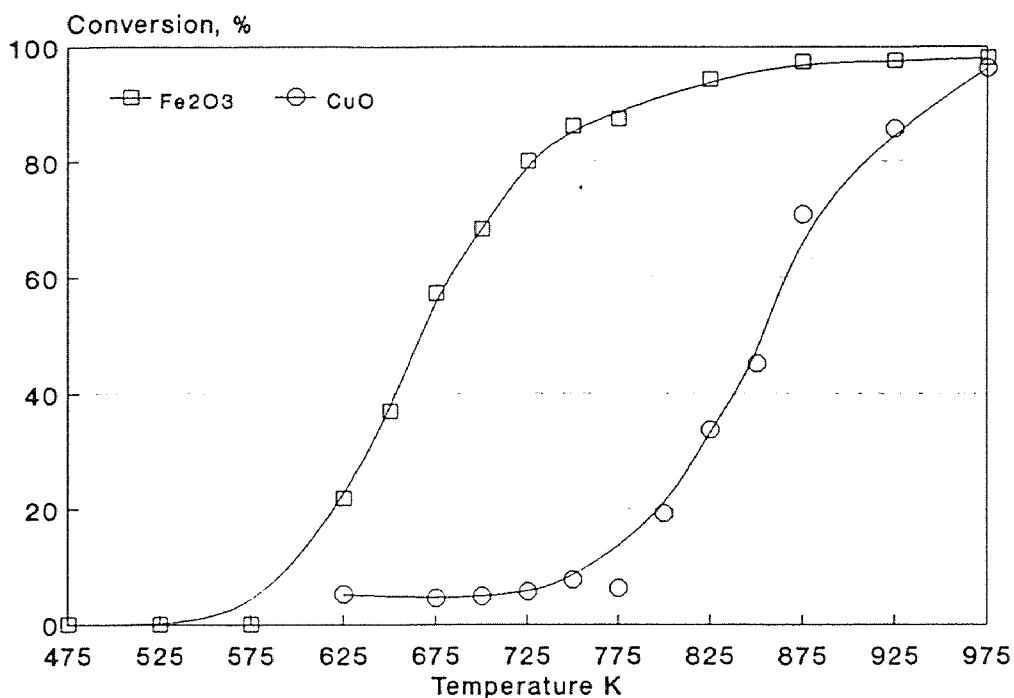

Figure 14. Conversion of 100 ppm TCE as a function of temperature over Fe_2O_3 or CuO

4.4.4 Kinetic Studies of TCE Oxidation over Fe_2O_3

In these experiments, the initial concentration of trichloroethylene was approximately 100 ppm , different space velocities were used for each case, and air was employed as the oxidant. For kinetics studies, the measured rates of oxidation of trichloroethylene in air are correlated first using the empirical power law as the form:

$$-r_{C2HCl3} = k' \, C_{C2HCl3}{}^a \, C_{O2}{}^b \qquad (4)$$

Where: C_{C2HCl3} and C_{O2} are the concentrations of trichloroethylene and oxygen, respectively. Since the experiments were conducted in large excess of oxygen, one can assume the concentration of oxygen is constant and a pseudo rate constant can be measured that incorporated the concentration of oxygen. One can further assume that the oxidation of trichloroethylene is first order with respect to trichloroethylene. This, of course, must be verified experimentally.

In order to keep the reaction in the chemical kinetics controlled region, all data were collected at conversions less than 30%. The conversions of trichloroethylene as a function of temperature over iron oxide at different residence times are shown in Figures D1 and D2 (appendix D). The linearity of the plots of logarithm of the (Co/C) versus residence time shown in Figure 15 confirm that the oxidation of trichloroethylene over iron oxide is a first order reaction.

According to the Arrhenius equation:

$$k = A \exp (-Ea/RT) \qquad (5)$$

Where: A is the preexponential factor,

         Ea is activation energy, kcal/mole,

         R is gas constant, kcal/mole * K

         T is absolute temperature, K

then, $\ln k = \ln A + (-Ea/R) * (1/T)$

Figure 16 is a plot of the logarithm of the rate constant versus 1/T. The Ea and A were obtained from the slope and intercept. The activation energy, Ea, is calculated as 25.4 ± 1 kcal/mole and the preexponential factor, A, is $8.09\pm0.5 * 10^8$ sec^{-1}. So, the rate equation can be written:

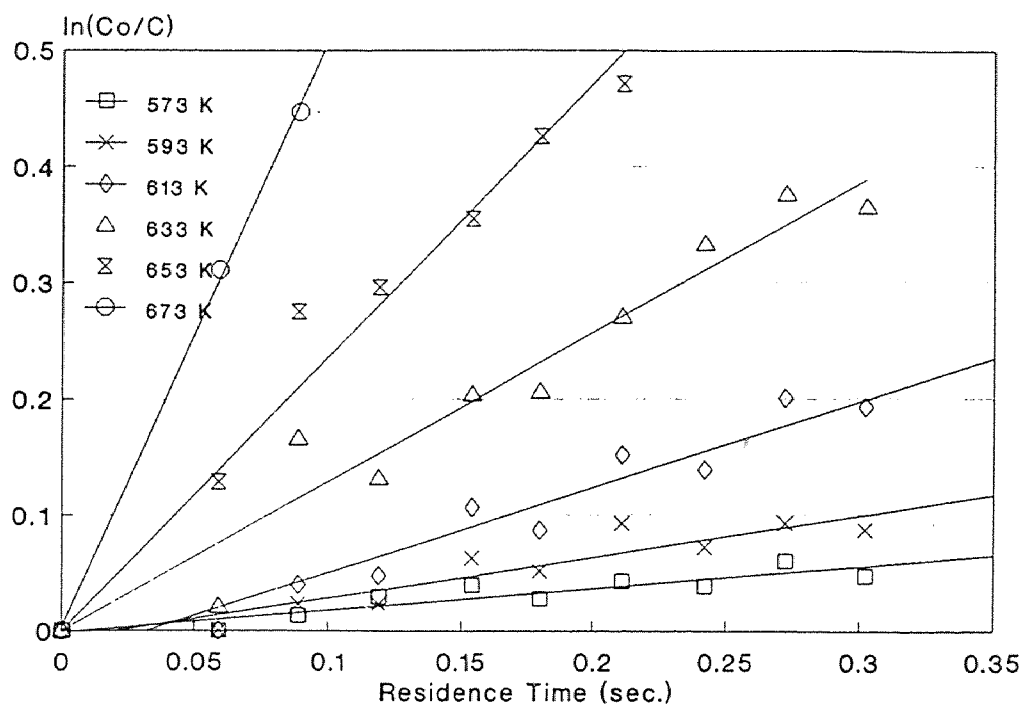$$-r_{C2HCl3} = 8.09\pm0.5 * 10^8 \exp (-25.4\pm1/RT) * C_{C2HCl3} \qquad (6)$$

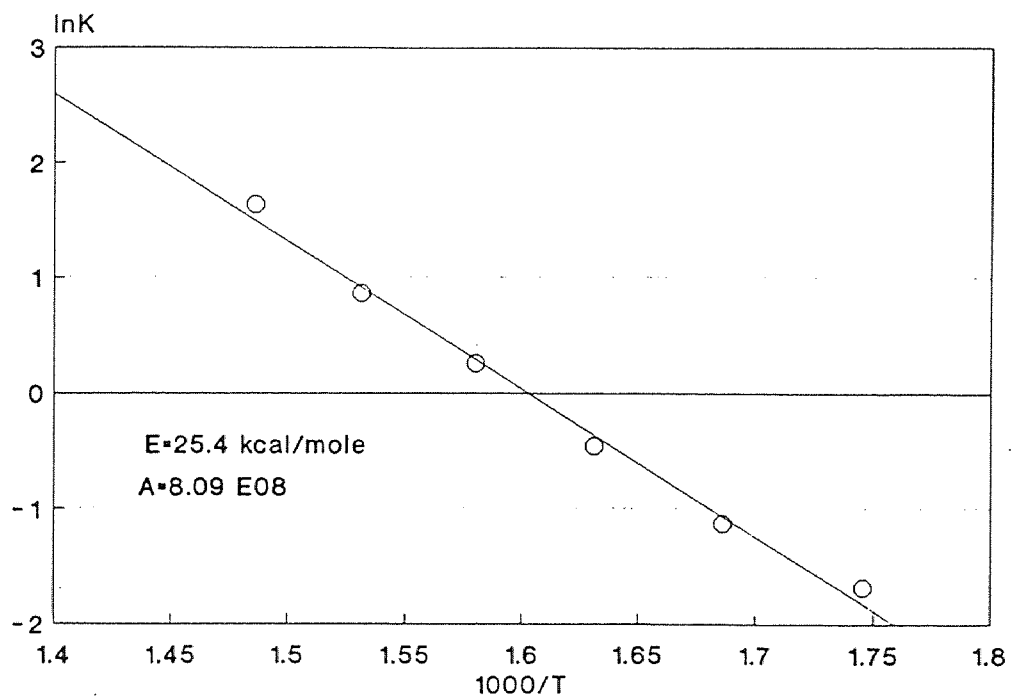**Figure 15** First order rate constant for TCE oxidation over Fe_2O_3

Figure 16 Arrhenius plot of first order rate constant for TCE oxidation over Fe_2O_3

4.4.5 Product Distribution and Material Balance of TCE Oxidation over Fe_2O_3

The product distribution of catalytic oxidation of trichloroethylene over iron oxide was conducted in the temperature range of 300 to 900 K, and at the indicated space velocity of 17,400 v/v/hr and the initial concentrations of trichloroethylene 111 ppm. The dependence of product distribution on temperature is plotted in Figure 17, the product distribution, material balances for carbon and chlorine are summarized in Table 4. The main products are carbon dioxide, carbon monoxide, hydrogen chloride and chlorine. Trace amounts of tetrachloromethane and perchloroethylene are also produced. At the lower oxidation temperature, the concentration of carbon monoxide increases with increasing temperature. At a temperature of 713 K, the concentration of carbon monoxide reaches a maximum and then decreases with increasing temperature. The distributions of tetrachloromethane and perchloroethylene follow a similar trend to that of carbon monoxide. Table 4 also shows the excellent carbon balances and chlorine balances of trichloroethylene oxidation.

Table 4 Materials Balance of TCE Oxidation over Fe_2O_3

| Temp.	C2HCl3	CO	CO2	CCl4	C2Cl4	HCl	Cl2	Carbon	Chlorine
K	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Balance	Balance
298	111.0	--	--	--	--	--	--	100	100
495	112	--	--	--	--	--	--	100±10	100±10
551	109.1	--	--	--	--	--	--	100±10	100±10
606	103.7	18.7	0	0.02	0	41.3	0	101.1±10%	105.0±10%
660	54.9	66.0	46.4	0.03	0.51	93.5	33.3	99.8±10%	97.4±10%
713	16.1	91.1	88.0	0.05	0.38	105.1	78.7	94.7±10%	93.1±10%
765	4.3	65.9	134.1	0.06	0	109.2	90.2	93.2±10%	90.2±10%
815	2.7	40.2	159.3	0.23	0	113.9	98.0	91.6±10%	95.0±10%
915	0.6	13.4	188.8	0.05	0	124.5	111.6	90.9±10%	104.1±10%
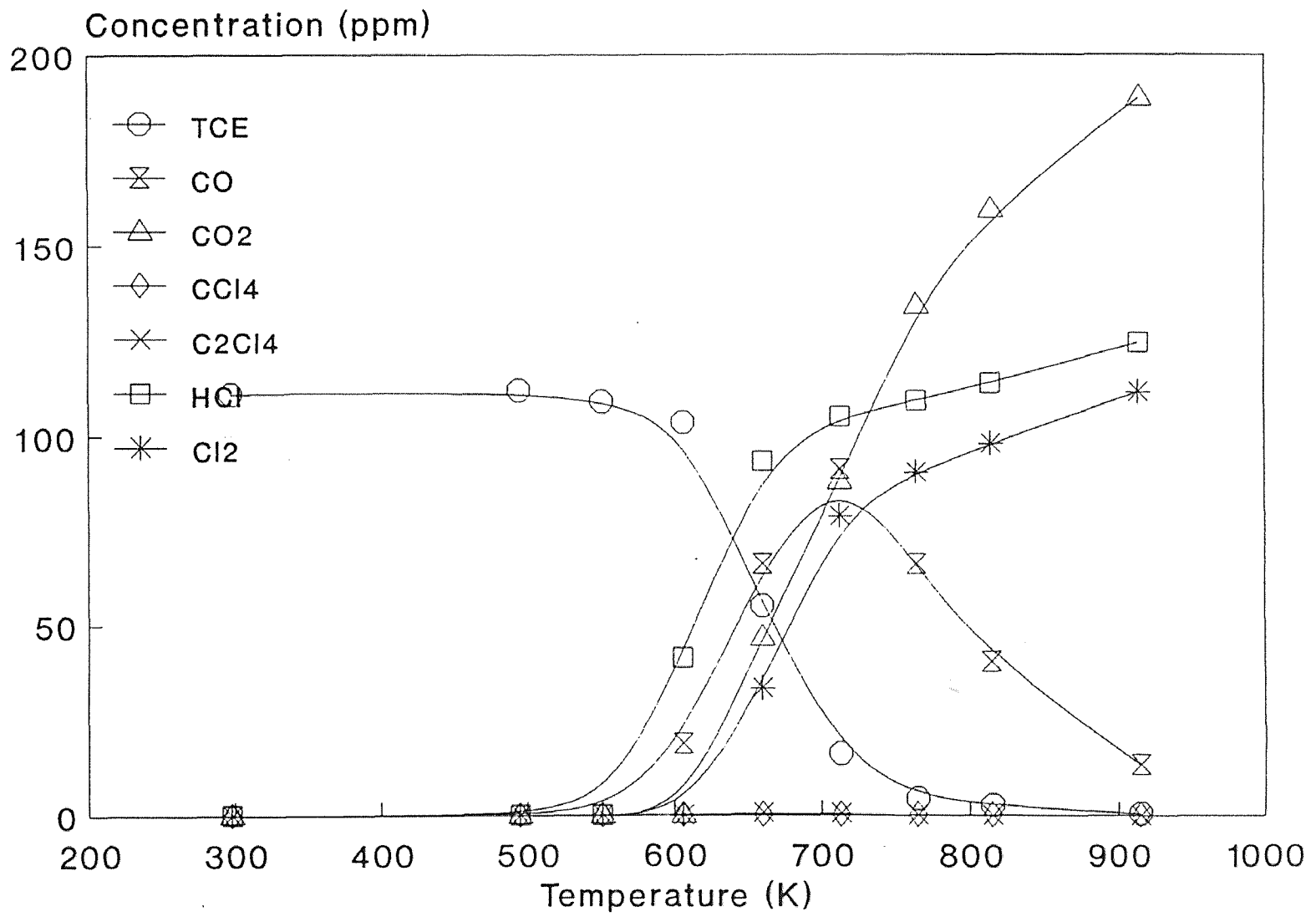
Figure 17 Products distribution of TCE oxidation over Fe_2O_3

4.4.6 Water Additive Effect on TCE Oxidation

Trichloroethylene contains only one hydrogen atom. Consequently, upon complete oxidation, TCE would yield equal molar concentrations of hydrogen chloride and chlorine. Since chlorine is a toxic gas that is not easily collected, it is desirable to inhibit the formation of chlorine gas and enhance the selectivity to hydrogen chloride. Therefore, a common hydrogen source, water, was added. It has been suggested that water can easily dissociate on the oxygen-precovered surface of the catalyst which provide hydrogen atoms to react with chlorinated hydrocarbons at low temperatures (Heras and Viscido, 1988). Alternatively, a mechanism can be written that includes surface gas phase reactions of Cl atoms with water to give HCl and OH (Narayanan, et al., 1990). The results of product distribution and material balance of the catalytic oxidation of trichloroethylene with the addition of water is summarized in Table 5. It is observed that no significant amount of chlorine gas is detected, the selectivity to hydrogen chloride is enhanced dramatically.

Table 5 Materials Balance of TCE Oxidation over Fe_2O_3 in the Presence of Additive H_2O

Temp.	C2HCl3	CO	CO2	CCl4	C2Cl4	HCl	Cl2	Carbon	Chlorine
K	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Balance	Balance
298	99.0	--	--	--	--	--	--	100	100
658	39.9	43.7	63.7	0.11	0.72	155.2	0	95.3±10%	93.7±10%
712	10.2	56.8	101.4	0.25	0.54	234.9	0	90.8±10%	90.4±10%

CHAPTER 5

CONCLUSIONS

As a consequence of the research, the following conclusions were reached:

• The light-off temperature for catalytic oxidation of 200 ppm dichloromethane over MnO_2 powder at 30,000 v/v/hr is 500 K, and 74% is the highest conversion which can be achieved at 700 K.

• The main products from the catalytic oxidation of dichloromethane over MnO_2 are carbon dioxide, chlorine, hydrogen chloride. The by products from the catalytic oxidation of dichloromethane over MnO_2 are tetrachloromethane and chloroform.

• Both carbon and chlorine balance for oxidation of dichloromethane over MnO_2 at the space velocity of 30,000 v/v/hr and at temperature 605 K and 663 K are satisfied within $100\pm10\%$.

• The surface area of Fe_2O_3 powder catalyst measured by BET method is 6 ± 2 m^2/g and the surface area of CuO powder catalyst measured by BET method is less than 3 m^2/g.

• The products of catalytic oxidation of trichloroethylene over transition metal oxides are carbon dioxide, carbon monoxide, chlorine and hydrogen chloride, water and trace amounts of tetrachloromethane and perchloroethylene.

• The light-off temperature for catalytic oxidation of 100 ppm trichloroethylene over Fe_2O_3 powder at 12,000 v/v/hr is 570 K, and 99% conversion is achieved at 915 K. The light-off temperature for catalytic oxidation of 100 ppm trichloroethylene over CuO powder at 12,000 v/v/hr is 770 K, and 96% conversion is achieved at 970 K. Fe_2O_3 catalyst is more efficiency for oxidizing trichloroethylene than CuO catalyst.

• The main products from the catalytic oxidation of trichloroethylene over Fe_2O_3 are carbon dioxide, carbon monoxide, chlorine and hydrogen chloride. However, trace

amounts of tetrachloromethane and perchloroethylene as intermediate products are also found.

• Both carbon and chlorine balance for oxidation of trichloroethylene over Fe_2O_3 at the space velocity of 17,400 v/v/hr at six different temperature are satisfied within $100\pm10\%$.

• The oxidation reaction of trichloroethylene obeys first order reaction kinetics with respect to trichloroethylene.

• The activation energy, Ea, for the oxidation of trichloroethylene over Fe_2O_3 powder is 25.4 ± 1 kcal/mole, and the preexponential factor, A, is $8.09\pm0.5*10^8$ sec^{-1}.

• When water was added to the feed stream, it slightly accelerated the oxidation reaction of trichloroethylene, and improved selectivity to hydrogen chloride.

APPENDIX A

BET SURFACE AREA RESULTS

27938

SAMPLE NAME: CUO
ADS. SURFACE AREA 19 m2/g
DES. SURFACE AREA 0 m2/g

$$\frac{1}{X[Po/P-1]}$$

ADSORPTION PLOT +
DESORPTION PLOT o

0

.1   .2   .3

P/Po

Figure A1 BET plot for CuO powder
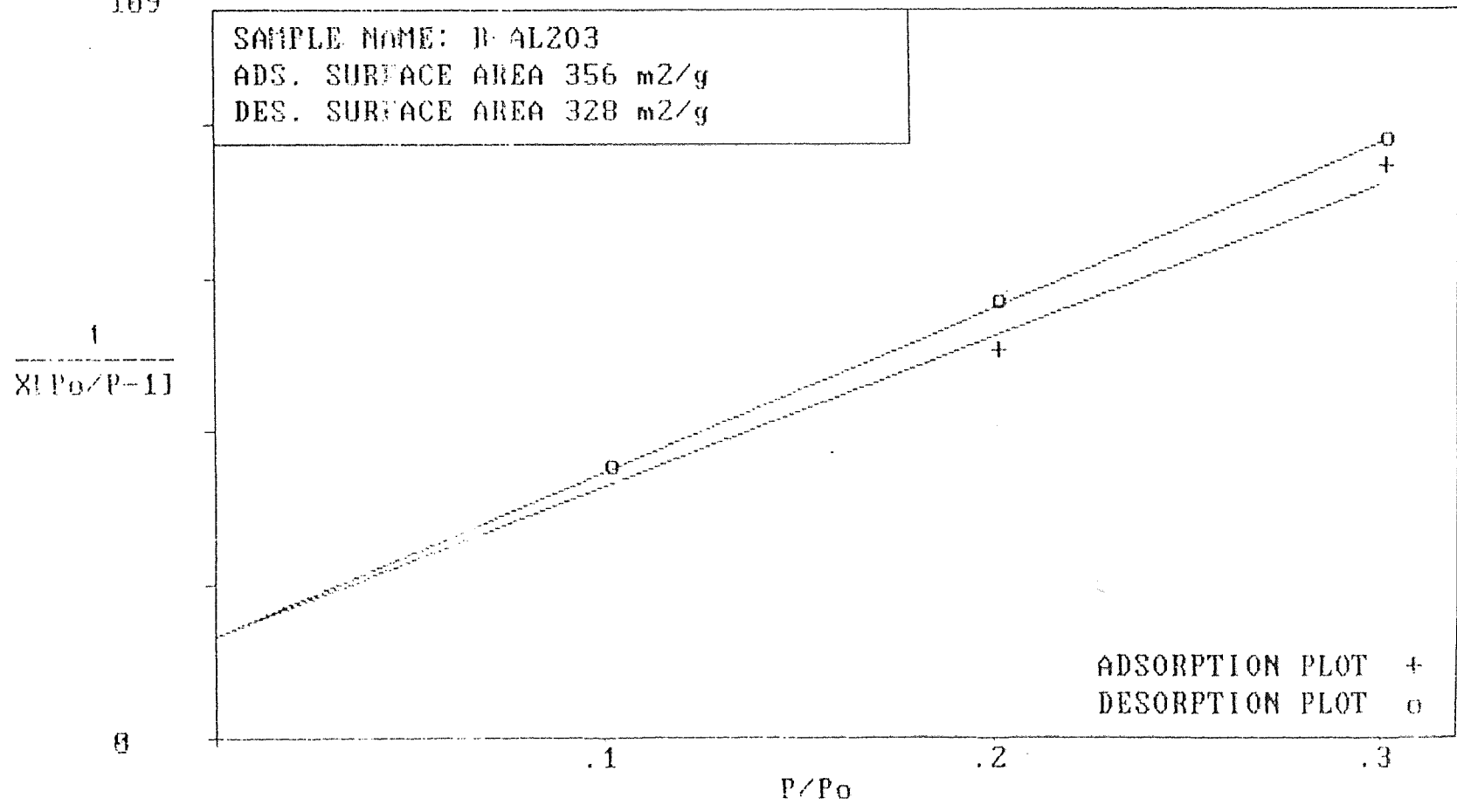
Figure A2 BET plot for β-Al$_2$O$_3$ powder

APPENDIX B

GC/MS OF REACTION PRODUCTS

Figure B1 Mass spectrum of CCl$_4$

Comment:
Average of: 336 to 343   Minus: 343 to 343   100% = 2706
100%   95

132

SMP

—

BKG

33

60

47

82

157 173 189   216 231   258 271 286

20   40   60   80   100   120   140   160   180   200   220   240   260   280   300
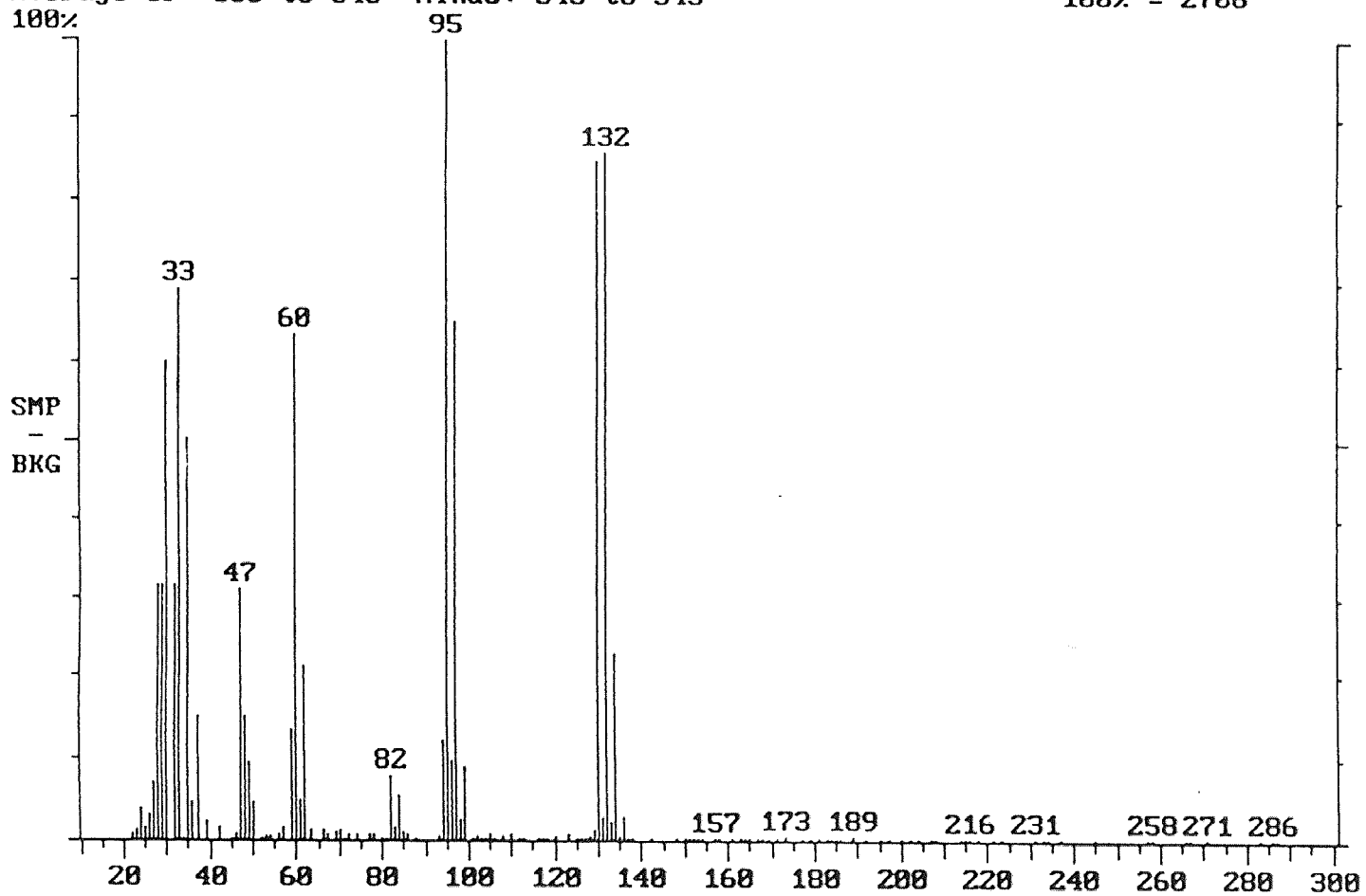
Figure B2 Mass spectrum of C_2HCl_3
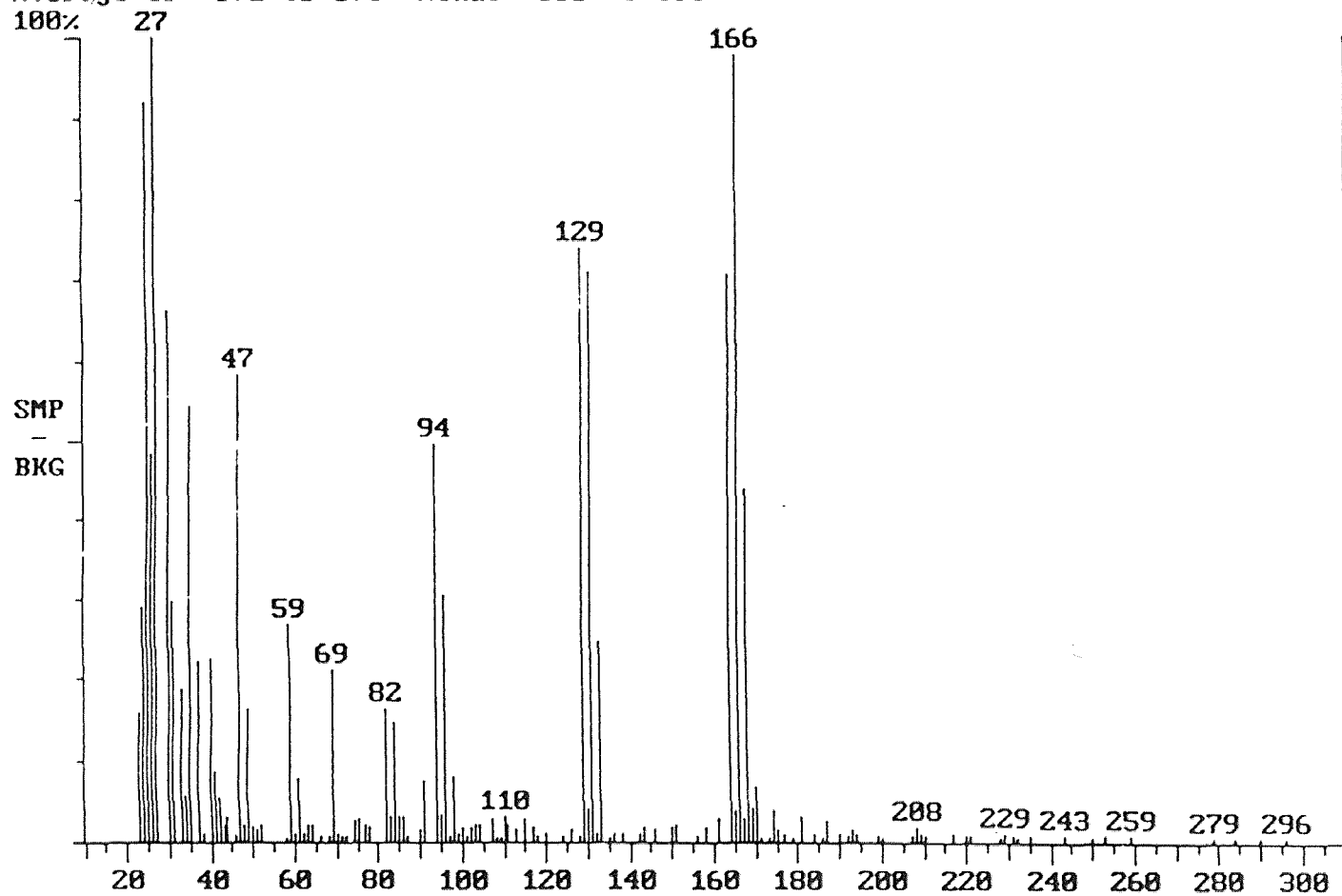
Figure B3 Mass spectrum of C_2Cl_4
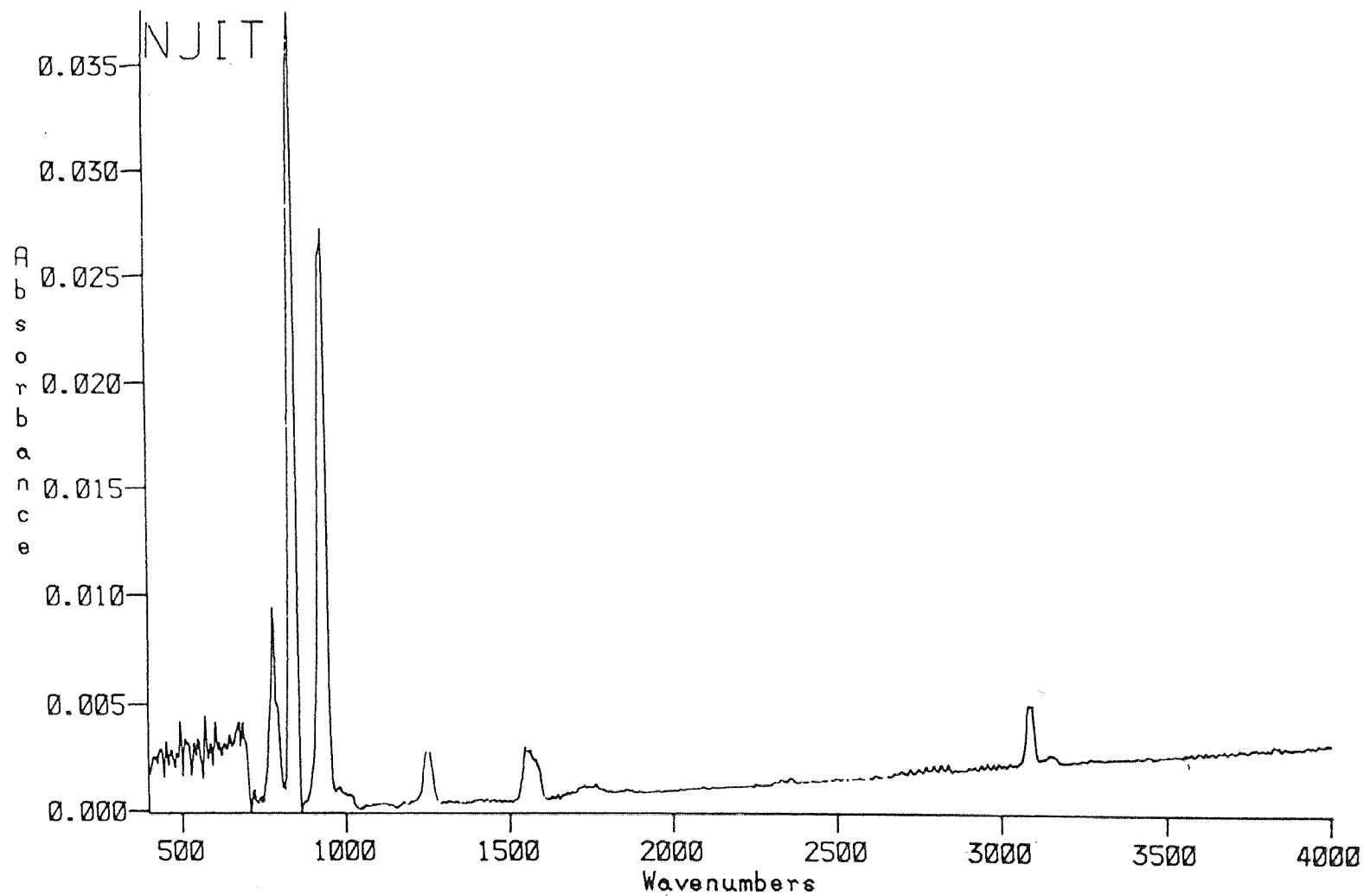
APPENDIX C

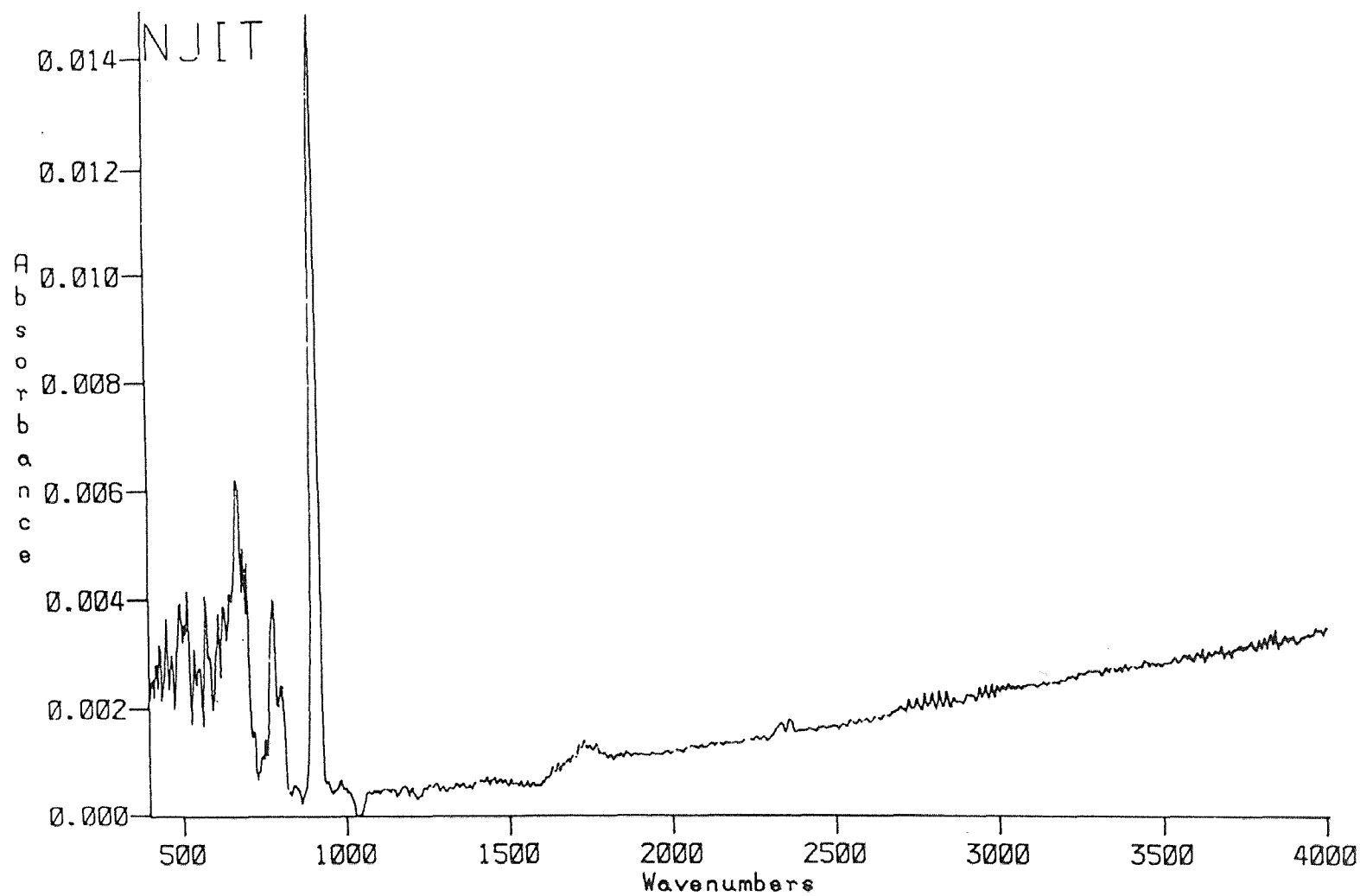## GC/FTIR OF REACTION PRODUCTS
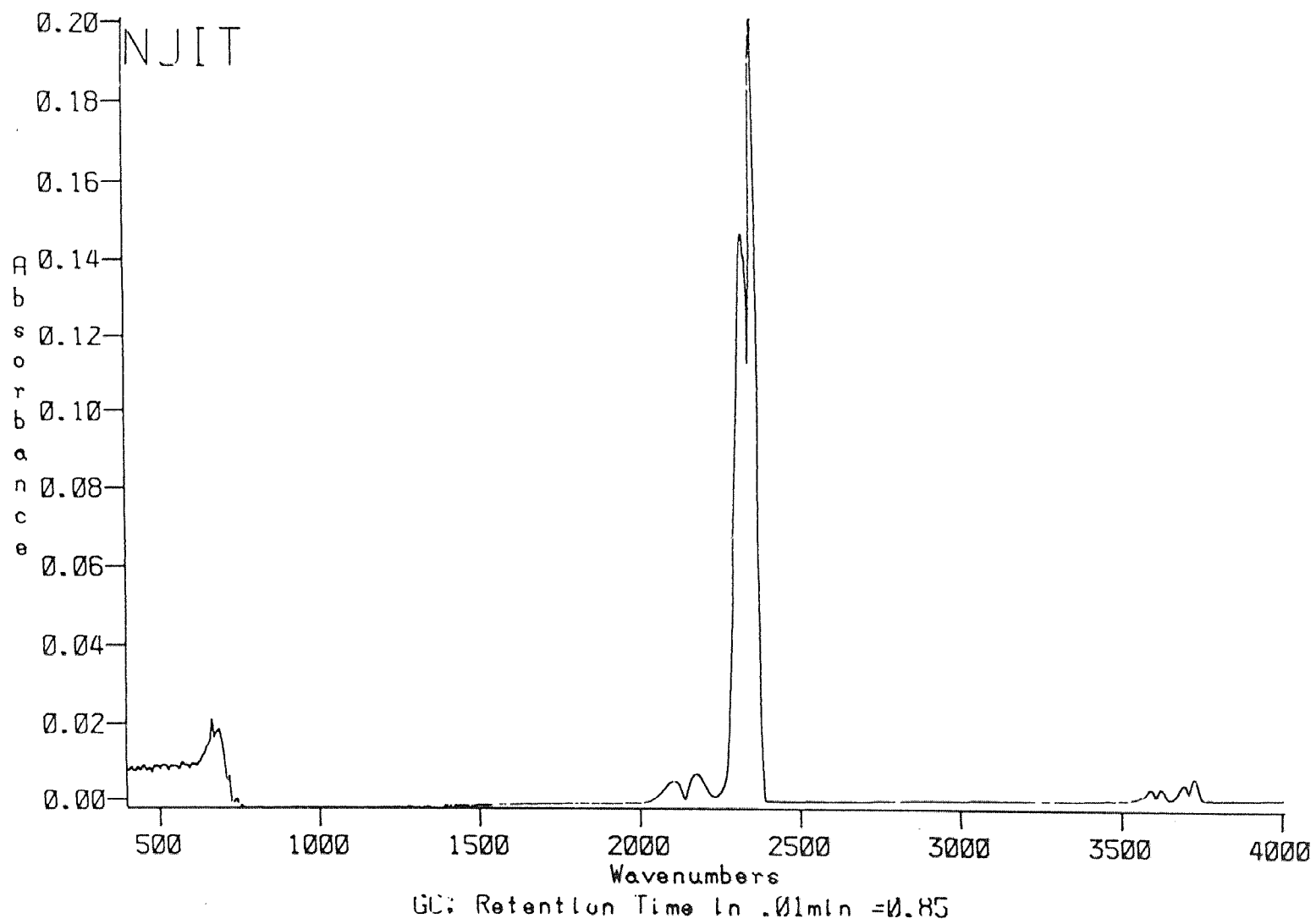
Figure C1 Infrared spectrum of CO_2
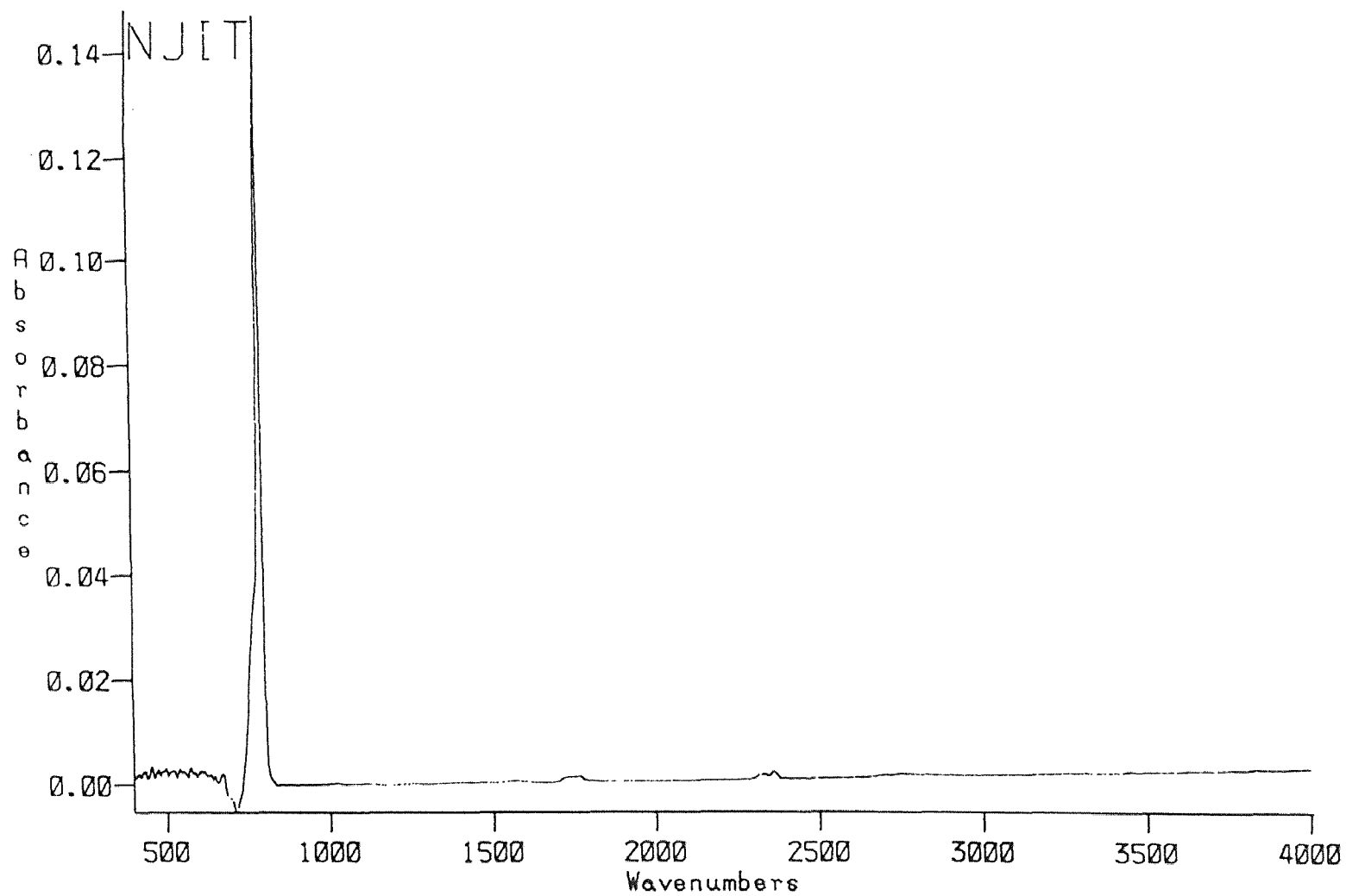
Figure C2 Infrared spectrum of CCl_4

Figure C3 Infrared spectrum of C_2HCl_3

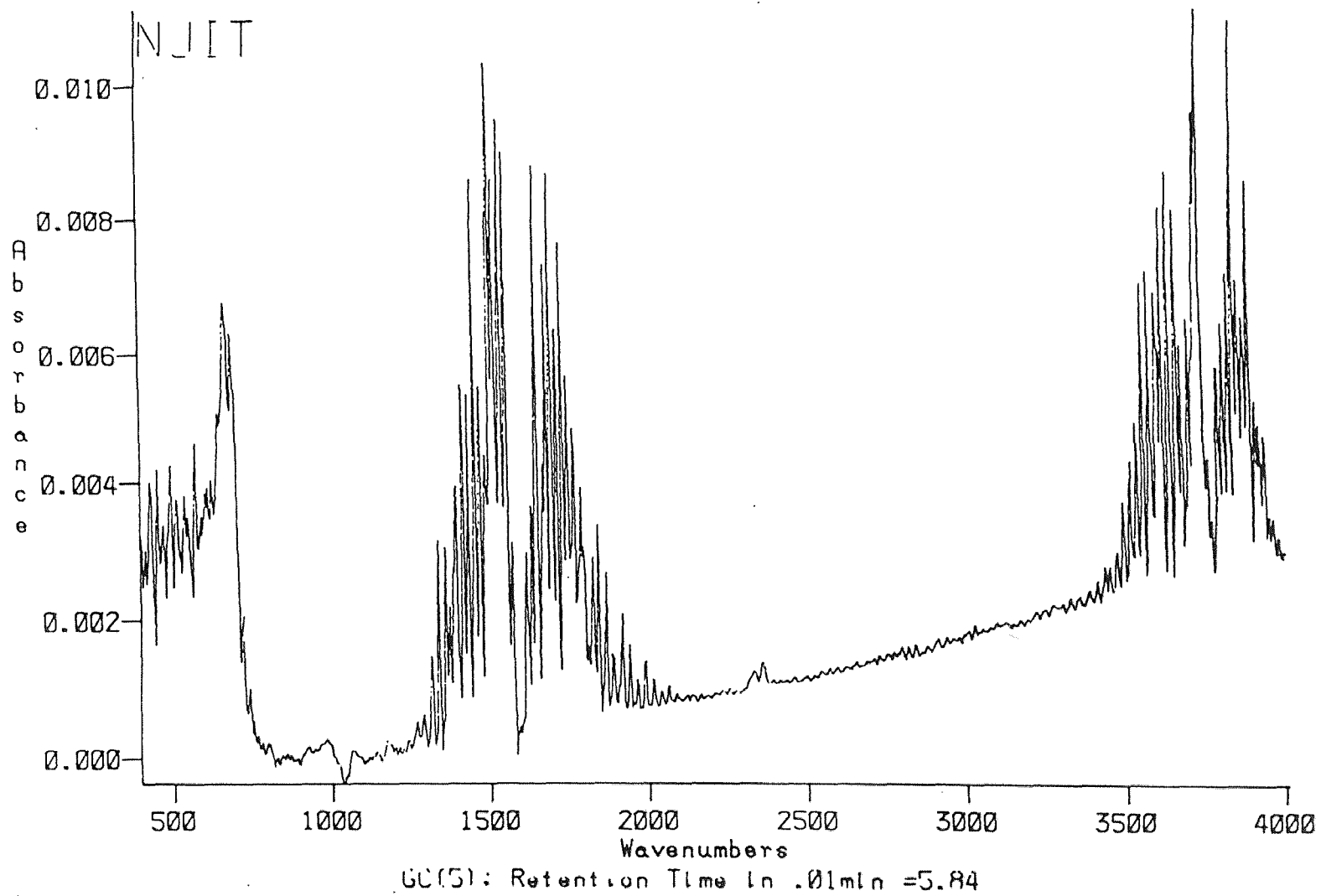**Figure C4** Infrared spectrum of C_2Cl_4

Figure C5 Infrared spectrum of H_2O
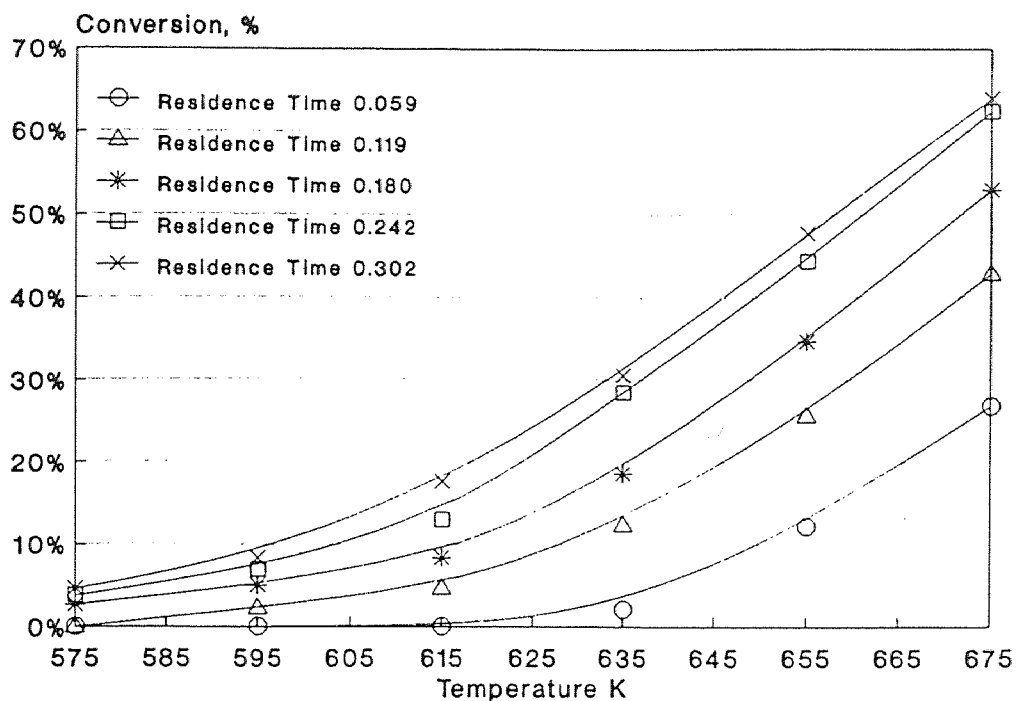
APPENDIX D

KINETIC RESULTS

Figure D1 Conversion of TCE as a function of temperature over Fe_2O_3 at different residence times (I)
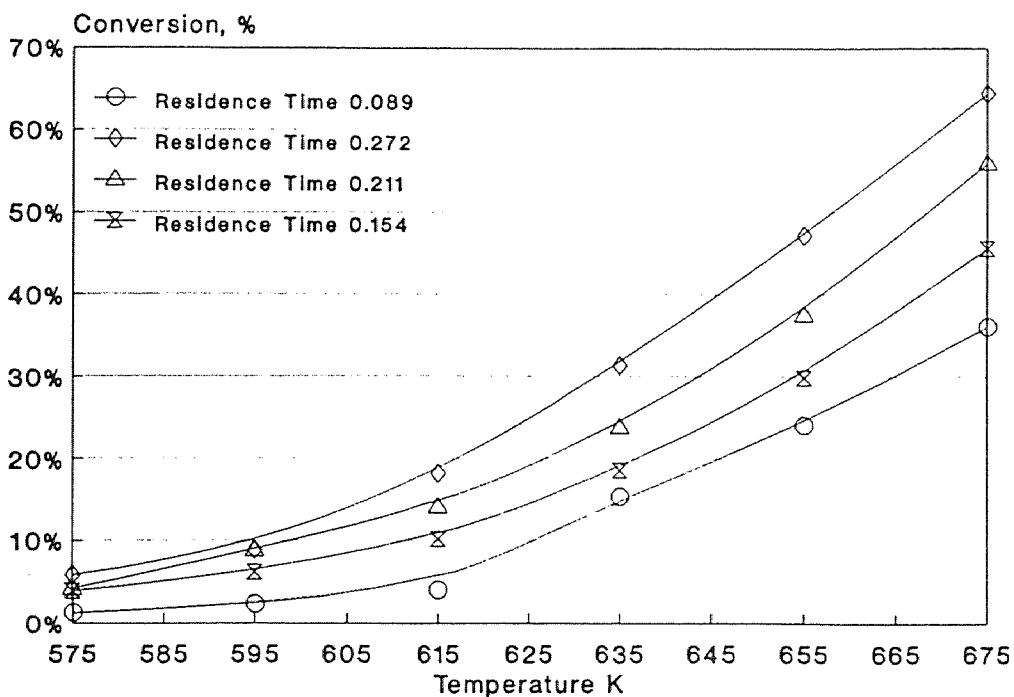

Figure D2 Conversion of TCE as a function of temperature over Fe_2O_3 at different residence times (II)

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